PB87-168761

Dewatering of Dilute Aqueous Hazardous Wastes Using Reversible Gel Absorption

Minnesota Univ., Minneapolis

Prepared for

Environmental Protection Agency, Cincinnati, OH

Mar 87

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/2-87/020	2.	3. RECIPIENT'S ACCESSION NO. PB87-168761/AS
4. TITLE AND SUBTITLE Dewatering of Dilute Aqueous Hazardous Wastes Using Reversible Gel Absorption		5. REPORT DATE March 1987 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Walter J. Maier, Edward L. Cussler		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Minnesota, Minneapolis, MN 55455		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-03-1957
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

The feasibility of using [illegible]linked gels in a reversible process for extracting pure water from aqueous waste [illegible]ons has been investigated. It has potential for concentrating waste streams that contain hazardous chemicals. Near critical gels have been developed which swell and collapse as a function of process conditions. At low temperature or high pH, these gels swell by absorbing water. During swelling, they exclude larger solutes, including many hazardous materials. Solutes and colloidal pollutants thus may be concentrated to facilitate treatment and disposal. The gels are made from water soluble monomers; they can be easily regenerated by warming or by adding acid to release the purified water. The collapsed gels are separated by filtration and reused.

In this study gels have been contacted with solution containing a wide range of different molecular weight solutes and colloids to determine water extraction capacity and efficiency of solute rejection.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 95
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB87-168761

EPA/600/2-87/020
March 1987

DEWATERING OF DILUTE AQUEOUS HAZARDOUS WASTES USING REVERSIBLE GEL ABSORPTION

by

Walter J. Maier
Civil and Mineral Engineering

Edward L. Cussler
Chemical Engineering

University of Minnesota
Minneapolis, MN 55455

68-03-1957

Project Officer:

Mark J. Stutsman
Hazardous Waste Engineering Research Lab
Alternative Technologies Division
Cincinnati, Ohio 45268

Hazardous Waste Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies, industrial products, and practices frequently carry with them the increased generation of aqueous hazardous waste streams. These materials, if improperly dealt with, can threaten both public health and the environment. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically. To further these objectives, EPA has provided partial funding of research aimed at developing innovative separation processes.

This report describes the results of research on a new process for concentrating aqueous waste streams using gels to extract water. The gels are recovered and reused in a cyclic manner. This type of processing is potentially useful for treating aqueous streams with low concentration wastes in order to facilitate ultimate disposal of the wastes and for recycle of water to minimize dispersion of pollutants into the environment.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The feasibility of using crosslinked gels in a reversible process for extracting pure water from aqueous waste solutions has been investigated. It has potential for concentrating waste streams that contain hazardous chemicals. Near critical gels have been developed which swell and collapse as a function of process conditions. At low temperature or high pH, these gels swell by absorbing water. During swelling, they exclude larger solutes, including many hazardous materials. Solutes and colloidal pollutants thus may be concentrated to facilitate treatment and disposal. The gels are made from water soluble monomers; they can be easily regenerated by warming or by adding acid to release the purified water. The collapsed gels are separated by filtration and reused.

In this study gels have been contacted with solution containing a wide range of different molecular weight solutes and colloids to determine water extraction capacity and efficiency of solute rejection.

CONTENTS

Foreword....iii
Abstract....iv
Figures....vi
Tables....viii

1. Introduction....1
2. Conclusions....5
3. Recommendations....9
4. Literature Review....10
5. Gel Preparation, Methods and Analytical Procedures....15
6. Studies of Gel Volume....21
7. Selectivity of Gel Extraction....42
8. Process Studies....59
9. Summary - Conclusion....81
10. Future Work....83

References....84

FIGURES

Number		Page
1.	Phase Diagrams	3
2.	A Separation Process Based on Temperature Sensitive Gels	6
3.	Separation Process Using pH Sensitive Gel	11
4.	Graph of Concentration vs. Absorbance for Vitamin B12	18
5.	Graph of Concentration vs. Refractive Index Differences for PEG 400	18
6.	Graph of Concentration vs. Refractive Index Differences for PEG 3400	20
7.	Titration of Linear Polyacrylic Acid	20
8.	Dissociation Constant of Polyacrylic Acid	22
9.	Gel volume as a Function of Solution pH	24
10.	Acid Titration of Gel	25
11.	Gel Swelling Decreases with Increased Crosslinking	27
12.	Swelling as a Function of Crosslink Fraction and Acrylamide Concentration	28
13.	Gel Volume as a Function of pH of Solution Being Extracted	30
14.	Mole Ratios of Hydrogen Ions to Gel	32
15.	Effect of pH on Ionization of Carboxyl Groups in Polymeric Structures	35
16.	Gel Swelling Versus Salt Added	37
17.	Gel Swelling Versus Temperature	39
18.	Extraction Procedure for Determining Separation Efficiency	45
19.	Results of Vitamin B12 Extraction as a Function of Crosslink and Acrylamide Concentration in Gel	47
20.	Results of PEG 400 Extraction as a Function of Crosslink Acrylamide Concentration in Gel	48

21. Results for PEG 3400 Extraction as a Function of Crosslink and Acrylamide Concentration in Gels.....49

22. Separation Efficiency Depends on Solute Shape.....51

23. Effect of Crosslink Concentration on Efficiency.....57

24. Gelatin Concentration Effect Using Polyisopropylacrylamide.....57

25. EDTA Ionization Versus pH.....63

26. Gel Volume Versus Ionic Strength of External Solution.....66

27. Latex Concentration Over Several Gel Extraction Cycles.....76

28. Ion Exclusion Donnan Effect.....79

TABLES

Number

1. Solutes Successfully Separated by Gel Extraction.....7

2. Solutes That Are Less Successfully Separated by Gel Extraction.....8

3. Reagents for Gel Preparation.....15

4. List of Chemicals Tested.....17

5. Physical Chemical Composition of Gels.....26

6. Preparation of Acidified Gels.....29

7. Extraction of PCP Solution Using Acidified Gels.....33

8. Polyisopropylacrylamide Swelling vs. Added Acid and Salt.....38

9. Concentration of Aqueous Solutions Using Hydrolyzed Polyacrylamide Gels.....52

10. Separation of Charged Solutes with Partially Hydrolyzed Polyacrylamide Gels.....54

11. Selectivity of Extraction Using Temperature Sensitive Gels.....55

12. Solubility of Zinc in the Presence of Hydroxyl Ions.....60

13. Zinc Hydroxy Complexes.....61

14. Zinc Rejection Using pH Sensitive Gels.....64

15. Effect of pH on Zinc Rejection.....64

16. Solubility of PCP Versus pH.....67

17. Higher Gel Rejection Efficiencies at Low Concentrations.....68

18. Phenol Is Excluded at High pH.....69

19. PCP Extractions Using Initially Dry Gel.....70

20. Effect of NaOH Concentration on PCP Rejection.....72

21. Exclusion Efficiency of Selected Industrial Chemicals.....73

22. Gel Extraction of Solutions of Selected Industrial Chemicals.....74

SECTION 1

INTRODUCTION

The presently available technology for treating aqueous waste streams containing low concentrations of potentially hazardous materials is largely based on modifications of conventional physical-chemical unit processes that were developed for chemical manufacturing. Although they are effective, they are usually energy intensive, require chemical additions, or require high capital costs.

Innovative methods for concentrating dilute solutions are of particular interest because concentrates can be managed more easily. Concentration also facilitates reuse and recycle of materials in a closed system thereby minimizing disposal to the environment. Concentration of waste streams also facilitates ultimate disposal by incineration or physical-chemical treatments that would not be practical or economically feasible for large volume-low concentration wastewaters. Development of innovative methods for concentrating wastewaters was therefore deemed to be a desirable and practical objective.

The concept of dewatering wastewaters by extracting a water phase as opposed to extracting the solid waste material from solution-suspension has several potential advantages: Concentrate can be recycled; low volumes of concentrates can be treated more effectively and at lower costs; solidification is facilitated. As regards the extracted water phase, closed loop recycle of the water extract would minimize if not eliminate discharge of pollutants. The concept of dewatering waste streams as opposed to extracting the waste material from the water phase is technically sound because of the requirement for high efficiency (near 100%) of treatment. It is well known that essentially complete removal of pollutants from aqueous waste streams is technically difficult and becomes very costly at high per cent removals. By contrast, dewatering concentrates the waste and results in large volume reductions, thereby facilitating ultimate disposal of the chemicals. An additional advantage for dewatering is that it is applicable to a broad variety of wastes, whereas processes for extracting pollutants from a water phase are likely to be material specific.

The unique features that are needed for successful dewatering of aqueous waste streams include both technical and environmental considerations:

a) efficient sequestering of the water into a separate phase;
b) effective removal of the water containing phase;
c) simple processing requirements for release of water and recovery of sequestering agents;
d) low expenditure of energy and chemicals;
e) low overall capital cost;
f) broad applications to a variety of waste streams;
g) environmental acceptability, in that no new pollution problems are created;
h) safety for the personnel who may be involved as users of the dewatering process.

It is well known that small pore size membranes can be used to separate a water phase and retain concentrate by ultrafiltration or selective ion separation. While such membranes are effective for making separations, there are drawbacks. Membranes are usually quite expensive; they are susceptible to

plugging and deterioration; they require high pressures to force water through small pores. Furthermore, in membrane processes, solvent passes through membrane openings while larger or ionized molecules are restrained and accumulate in the retentate. The resultant accumulation of retained products results in layers of high solute concentration at the membrane surface and eventually slows flow through the membrane due to concentration polarization effects.

Recently published studies (6,28) have reported the use of water soluble gels to achieve essentially the same type of separation that can be obtained with membrane processes. The physical-chemical concepts that underlie gel extraction are related to the separation mechanisms encountered in molecular size ultrafiltration membrane separations, e.g., size exclusion, and ion selective membrane separations, e.g., ion exclusion. However, operational problems that stem from the need for high pressure and concentration polarization are overcome in gel separation because of the large surface area of the gels. Furthermore, the previous research on gels indicated that a reversible gel absorption process could be developed. This would allow reusing gels in a continuous process that meets the operating criteria listed above. Research on the development and use of gels was therefore undertaken.

This research had two objectives; the first was to develop near critical water soluble polymer gels which would swell and collapse in aqueous solutions with minor changes of temperature or pH; the second was to evaluate the effectiveness of these gels for concentrating dilute solutions of hazardous wastes.

The gels were made of substituted crosslinked acrylamides. One of the more successful temperature-sensitive gels is a polyisopropylacrylamide that was made by polymerization of N-isopropylacrylamide. Details of the synthesis are given in the body of the report; they closely imitate the procedures of other workers, especially those of Ilavsky (1). pH sensitive gels were made by polymerization and subsequent hydrolysis of acrylamide or by co-polymerization of acrylamide and sodium acrylate. The first of these syntheses is an expedited version of that described by Tanaka (2,3); the modified procedure described in this report takes about two hours instead of three months. The second synthesis which is described in Andrew's thesis (22) imitates those practiced commercially. With these two gels in hand, laboratory tests were set up to define mechanisms by which the gels worked, how much water they can imbibe and release, and what types of solute molecules and colloids would be rejected from entering the gel phase.

The theoretical background that explains the behavior of gels relates to behavior of solutions near a phase transition. Phase transitions are illustrated in Fig. 1. In the upper left hand corner of this figure, the phase diagram for a regular solution is shown as a plot of temperature *vs*. solute mole fraction x_2. The phase diagram is shaped like a parabola. Above this parabola, the system is a single phase; under the parabola, it is two phases whose compositions are exemplified by the ends of the horizontal dashed line. When a system of known concentration is cooled, it can initially be one phase and later become two phases, as suggested by the vertical dashed line.

The phase distribution of a regular solution as shown by the parabolic domains is a special case of solution behavior. The more general case is illustrated in the upper right hand corner of Fig. 1; it is the phase diagram for water-triethylamine. As before, the phase diagram consists of a plot of temperature *vs*. composition, which is expressed as a volume fraction ϕ_2. Like a regular solution, this system forms one phase at very high temperatures.

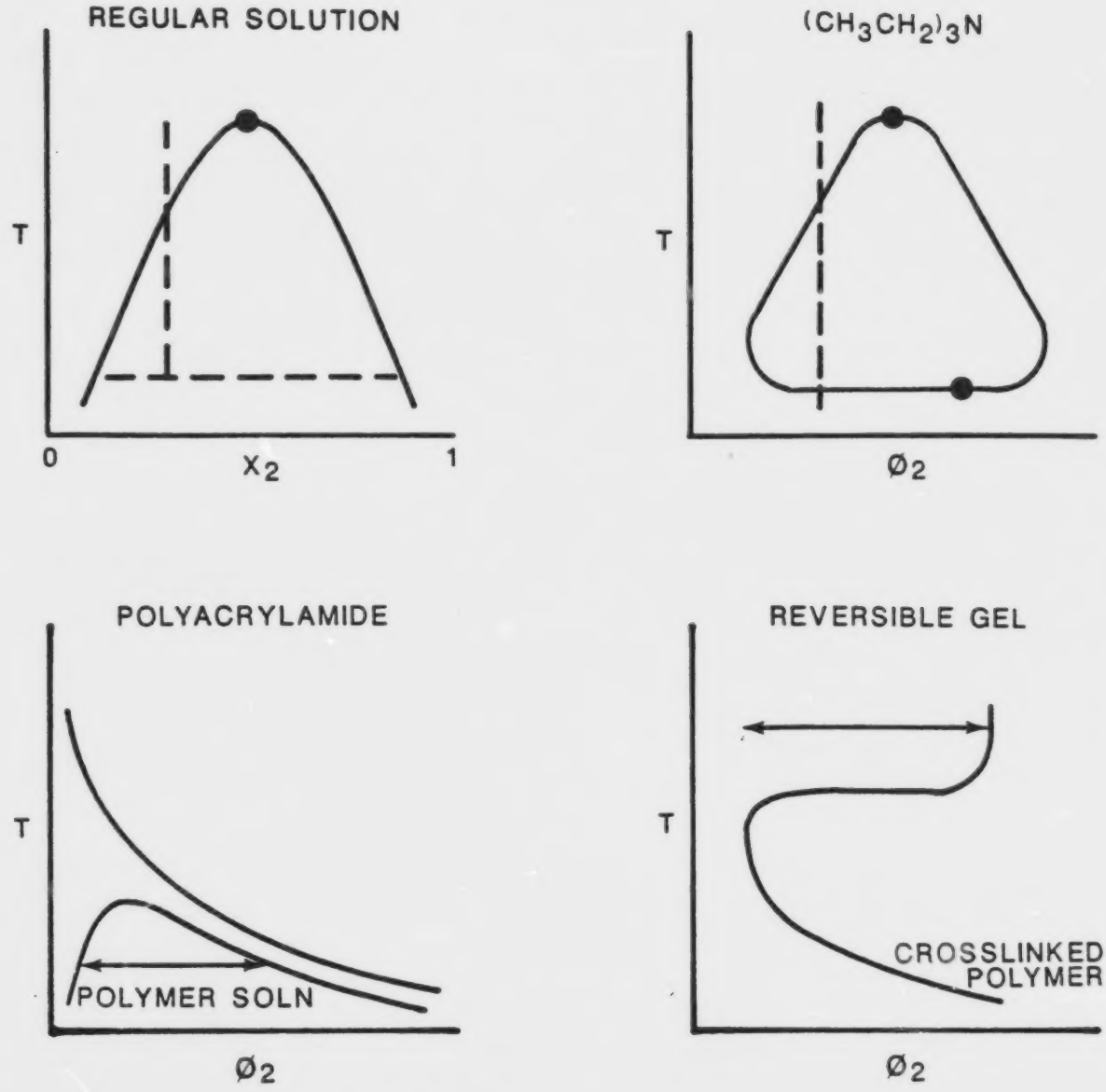


Figure 1 Phase Diagrams

T = temperature

$\emptyset_2$ = volume fraction

Unlike regular solutions it also forms one phase at low temperatures. In between, it forms two phases. When a solution of water-triethylamine containing one phase is cooled, it again follows a locus like the vertical dashed line. At high temperature it initially contains one phase. As it is cooled, it forms two phases. As it is cooled further, it forms one phase again. The behavior of a regular solution and of water-triethylamine is often discussed in terms of critical points, or, as they are more commonly called in liquid solution, consolute points. These consolute points are shown as the heavy black dots in Fig. 1. A regular solution forms only one consulate point, called an upper consolute point.

These same concepts have been extended to describe the behavior of water soluble polymers. For uncrosslinked polyacrylamides, the phase diagram is shown in the lower left hand corner of Fig. 1. This phase diagram again plots temperature vs. composition expressed as volume fraction ϕ_2. the phase diagram for the uncrosslinked polyacrylamide, shown by the lower of the two curves, looks like a regular solution, which has been bent strongly to the left. This bending is a consequence of the polymeric chains, which imply a solute of dramatically different molecular weight than the solvent.

However, if the polyacrylamide is crosslinked like our gels then the phase diagram is like the upper curve. At low temperature, the upper curve is similar to the lower curve for an uncrosslinked polymer. However when ϕ_2 is small, that is, when the polymer is dilute, the uncrosslinked polymer dissolves completely in the solvent. The crosslinked polymer swells to a maximum value. As a result a crosslinked polyacrylamide never fully dissolves, and its phase diagram shoots upwards.

The polymers used in this study can be represented by the superposition of the phase diagram for the crosslinked polyacrylamide and the phase diagram for triethylamine-water. At low temperatures, the phase diagram is like that shown in the lower left hand corner, but at high temperatures the phase diagram follows the schematic shown in the upper right hand corner. Overall behavior is characterized by a phase diagram like that shown in the lower right hand corner of Fig. 1.

Gels that have a phase diagram like that in the lower right hand corner of Fig. 1, would be expected to show temperature related volume changes as described in the experimental results of this report. In particular, when the gel is warmed, ϕ_2 will get slightly smaller and the gel volume will get slightly bigger. However, at a critical higher temperature, ϕ_2 will get much bigger and the gel volume will get much smaller. In many cases, this volume change with temperature can be abrupt. For example, the crosslinked polyisopropylacrylamide polymer described in this report showed a 5 fold volume change over a temperature increase of only 0.1°C.

These models were used as a theoretical framework for analyzing and correlating data on volume changes of the gels. The models also gave insight on development of new gels and the physical configuration of the gels.

SECTION 2

CONCLUSIONS

The overall objectives of the project were to demonstrate the feasibility of using temperature or pH sensitive gels to separate water from solutions to concentrate them. The gels are effective for concentrating solutions of macromolecular solutes, and hence are a commercially attractive alternative to ultrafiltration. The gels are less effective for concentrating small solutes. The overall separation process of a temperature sensitive gel for extracting water, thereby concentrating the residual solution, is shown in Fig. 2. In the first step, solution to be separated is contacted with a bed of temperature sensitive gel beads. The gel beads swell, absorbing water, while excluding macromolecular solutes. The swollen gel and the concentrated raffinate are then separated by filtration. The concentrated raffinate becomes the product. When swollen gel itself is warmed, it collapses, releasing the absorbed solution. The collapsed gel is again removed from this solution by filtration, producing an extract which contains little if any macromolecular solute. The warmed collapsed gel is reused by cooling which starts the cycle over again.

Three types of gels have been tested to determine their ability to concentrate different solutes. Typical results are given in Table 1 for three gels. The first gel, A, is a non-ionic, temperature sensitive gel. Gel B is an ionic, temperature sensitive gel. The third gel, C, is an ionic, pH-sensitive gel. The first two columns of the table describe some of the solutes that have been successfully concentrated using at least one of the three gels. The separation efficiencies reported in the last three columns of Table 1 are calculated by dividing the concentration change actually observed by that expected from the gel volume change. For example, a 100% efficiency means the solute is completely rejected by the gel while 0% efficiency would result if the solute moved freely into the gel with the water. 100% efficiencies were never observed because traces of solution are trapped between gel particles when the swollen gel is removed by filtration.

Table 2, arranged parallel to Table 1, shows several lower molecular weight solutes which are separted less efficiently. Both tables are consistent with the idea of the gel as a polymer mesh: larger solutes are screened out while smaller solutes are not rejected as effectively. More complete listings of chemicals are presented in the text.

If we now look a pentachlorophenol (PCP) on row four of Table 2, we notice a discrepancy in the efficiencies reported for the three gels. At high pH, PCP is anionic and is effectively concentrated by the ionic gels, but not by the non-ionic gel. At low pH, PCP is non-ionic and is not separted by either gel. Rejection of anionic species was also observed with other solutes. It represents a second mechanism of exclusion that stems from the ionic character of pH sensitive gels. The rejection of ionic solutes has been described quantitively in terms of a modified Donnan equilibrium model analogous to membrane separations.

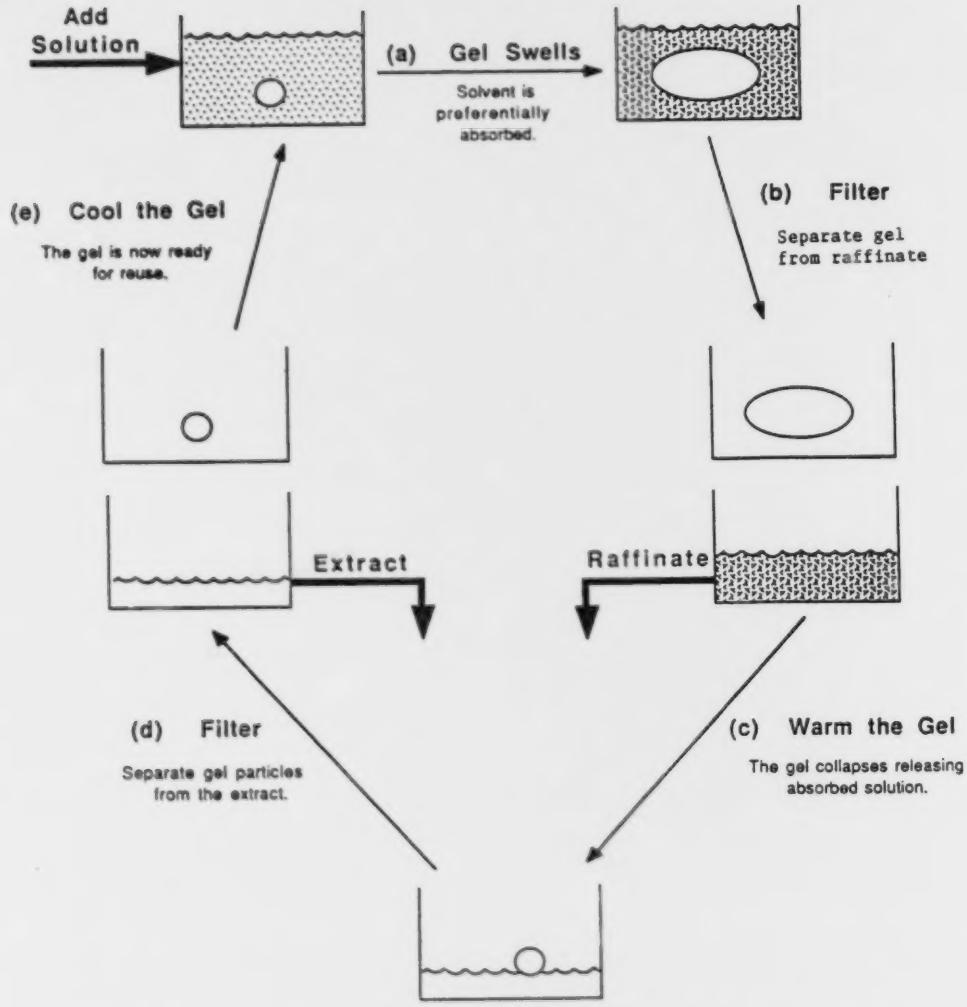


FIGURE 2: A Separation Process Based on Temperature Sensitive Gels

TABLE 1. SOLUTES SUCCESSFULLY SEPARATED BY GEL EXTRACTION

Solute	Molecular Weight	Separation Efficiencies* A	B	C
Albumin	45,000	97	84	93
Hemoglobin	64,500	--	--	91
Gelatin	65,000	98	97	--
Polyethylene Oxide	600,000	97	84	--
Blue Dextran	2,000,000	97	99	--
Polystyrene Latex	-----	95	96	82
Virus**	-----	80	--	85

*
A = n-Isopropylacrylamide Gel [1]
B = Diethylacrylamide/Acrylic Acid Copolymer Gel [1]
C = Hydrolyzed Polyacrylamide Gel [2,4]

**
A = Avian Flue Virus: 80% [3]
C = E. Coli: 85% [2]

TABLE 2: SOLUTES THAT ARE LESS SUCCESSFULLY SEPARATED BY GEL EXTRACTION

Solute	Molecular Weight	Separation Efficiencies* A	B	C
Vitamin B-12	1355	30	15	--
Polyethylen Glycol	400	10	5	--
Sucrose	342	--	--	6
Pentachlorophenol	267	18	86**	93**
Urea	60	2	3	0

* A = n-Isopropylacrylamide Gel [1]
B = Diethylacrylamide/Acrylic Acid Copolymer Gel [1]
C = Hydrolyzed Polyacrylamide Gel [2,4]

** Pentachlorophneol gave high separation efficiencies at pH above 7.5 but separation efficiencies were poor at lower pH levels because negative charge is neutralized by protonation.

SECTION 3

RECOMMENDATIONS

The use of gels for extracting relatively pure water has numerous possible practical applications for treating wastewaters. Potential applications include concentrating aqueous solutions to facilitate reuse-recycle of products, reducing volumes to facilitate storage and ultimate disposal, and extracting water to eliminate the need for discharging wastewater. However, further research and development are needed to fully exploit this separation technology.

The dynamics of swelling and contraction should be studied. The work described in this report was designed to analyze and describe water extraction capacities and rejection efficiencies at equilibrium. The time rate of change of gel expansion and contraction has not been studied. It has been observed that gel volume changes are very fast for small aggregates of gel. However, rates of water movement and exchange of ions by larger aggregates of gel should be studied in order to define mass transport limitations. A better understanding of the effects of gel aggregate size is needed in order to optimize process design conditions for contacting during the expansion and contraction cycle.

Process studies to evaluate the effects of staging should be carried out. Single stage extractions that involve large differences in concentration between gel phase and raffinate are thermodynamically unfavorable. Staged or sequential extraction would be more efficient and allow for more complete rejection of solutes from the extracted water phase.

Modified gels should be developed that combine the swelling and contraction characteristics of temperature sensitive gels with the solute rejection characteristics of the ionic gels. Such gels would be capable of rejecting ionic species as well as separating by molecular size. There are several advantages to using temperature cycles instead of pH changes to extract water; energy costs are low, there is no need for chemical addition, there is no increase in salt (ions) concentration. Another approach that should be pursued is grafting reverse osmosis membranes onto the outside of the gels themselves. Such grafting should provide the additional selectivity necessary for separating low molecular weight species like pentachlorophenol. Use of gels for other chemical systems including alcohol water and linear *vs*. branched alkanes should also be investigated.

SECTION 4

LITERATURE REVIEW

Gel-Water Interaction

The formation of a separable and physically measurable gel phase when water soluble monomers are polymerized into large interconnected three dimensional structures is a commonly observed phenomenon. Numerous polymeric materials possessing the ability to swell in water without dissolving have been described in the literature (4,5). Swelling is a consequence of the affinity of the chemical structure of the gel for water. Swelling is also affected by the degree of cross-linkages and the potential for ionization. Cussler et al. (6) suggested that appropriately cross-linked, partially hydrolyzed polyacrylamide gels could serve as selective extraction agents because these gels have unusual swelling characteristics. Such gels absorb water (a low molecular weight solvent) but reject high molecular weight solutes that are larger than the average pore diameter of the hydrogel. The gels can be regenerated by imposing a small change in process conditions such as pH (7), temperature (1,8), electric field (9), solvent composition (1,8,10), or salt concentration (11). These changes cause the gels to collapse, thereby releasing much of the water phase.

It has been shown that dramatic changes in volume occur as a result of small changes in process conditions when some of the side groups of the gel network undergo ionization. Ionization sets up localized negative charges. Small numbers of charge sites, around 1% (12), are effective. The resultant ionic matrix therefore expands and imbibes water while excluding macromolecules by steric exclusions and excluding ions by Donan exclusion.

Gel Extraction Process

The manner in which pH sensitive gels are used in an extraction process is illustrated in Figure (3). Gel material is added to the wastewater solution. The gel swells by absorbing water but excluding high molecular weight solutes. The raffinate solute concentration increases accordingly., It can be separated from the swollen gel by draining or filtration. The swollen gel is now regenerated by adding acid. Since the gel volume is very sensitive to pH change, it collapses and releases the absorbed water. The collapsed gel is again drained-filtered to remove water. Finally, the acidified gel is neutralized with a small amount of base, enabling it to swell again when added to another batch of solution.

The first part of this process, concentrating macromolecular solutions by allowing gels to swell in them was first reported by Flodin et al. (13). Specific applications have developed sporadically since then (4,11,14). Despite its success in concentrating solutions, the technique was limited in application due to the lack of an efficient method for regenerating the gel (drying was the only means). The swelling and collapse behavior of the gels in solvent, has been studied primarily as a type of phase transition behavior (12,15,3). Interest in this area was accelerated by Tanaka's 1978 (16) report of a discrete change in gel volume with an infinitesimal change in solvent composition.

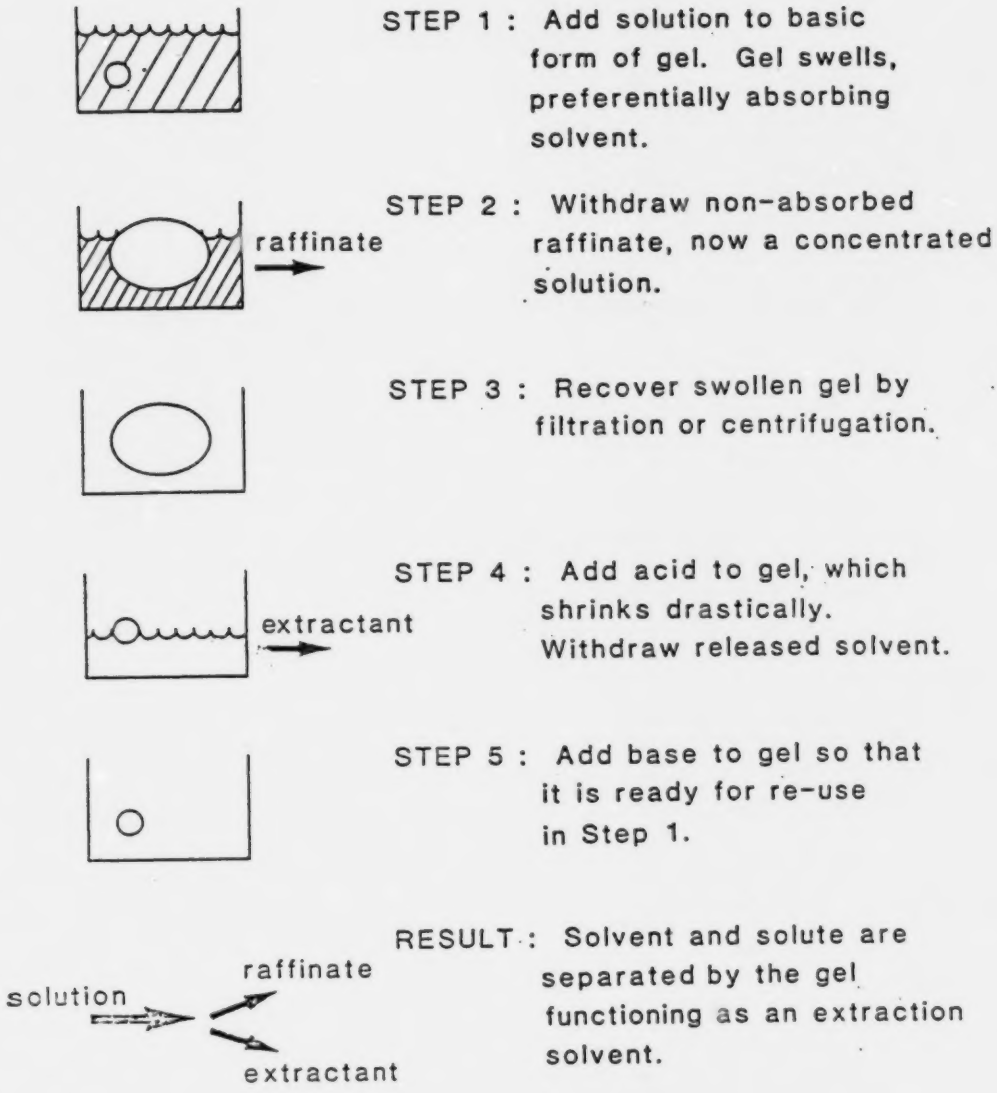

STEP 1 : Add solution to basic form of gel. Gel swells, preferentially absorbing solvent.
raffinate
STEP 2 : Withdraw non-absorbed raffinate, now a concentrated solution.
STEP 3 : Recover swollen gel by filtration or centrifugation.
extractant
STEP 4 : Add acid to gel, which shrinks drastically. Withdraw released solvent.
STEP 5 : Add base to gel so that it is ready for re-use in Step 1.
RESULT : Solvent and solute are separated by the gel functioning as an extraction solvent.
solution
raffinate
extractant

Figure 3 Separation Process Using pH Sensitive Gels

Gel Phase Expansion-Contraction

Volume changes of a gel phase in contact with a water phase is directly related to the uptake or release of water by the three dimensional structure of the polymer. It is therefore important to have a quantitative understanding of the effects of major process variables that affect polymer structure and its interaction with the surrounding solution phase. Thermodynamic considerations have been used to describe polymer behavior in water solutions using modifications of Flory-Huggins theory for polymer solutions (7,12,17,18,19). Theoretical models that describe volume changes as a result of changes in ionic nature of the gel have also been described (12,3,20,21). It was deemed important to obtain a sound theoretical framework to describe the changes in gel phase volume that are affected by modification of the structure of the polymer both in terms of its monomer chemistry as well as the degree of crosslinkage. Insight on the effects of changing the chemical composition of the solution phase is equally important.

Theoretical models based on thermodynamics have been used to describe the behavior of gels in solution (20). Cussler et al. (6) have shown that the model can be simplified so that gel swelling properties can be described in terms of measurable properties of the water phase and the gel. Gel expansion in water is related to the degree of gel ionization (ç), volume of potential ions per dry gel volume (Z), the volume fraction of the gel (V) and gel elasticity (K). for highly swollen gels, the equation simplifies to:

$$\left(\frac{V}{V_{dry}}\right)^{-2/3} = \frac{K}{\xi Z} \qquad (1)$$

where V_{dry} represents the dry gel volume. The ratio V/V_{dry} is a measure of the gel's swelling capacity. Equation (1) shows that swelling characteristics are related to elasticity which in turn reflects the degree of crosslinkage. The term çZ shows that the concentration of charged sites in the gel has a strong effect on gel swelling.

The validity of equation (1) has been tested by preparing a series of gels with different elasticities. Elasticity was changed by making gels with different amounts of crosslinklages and by changing the total acrylamide concentration. Crosslinkage concentration affects the gel's three dimensional expansion capacity. Acrylamide concentration affects gel density.

The validity of equation (1) can also be tested by varying the ionic character of the gel. In polyacrylamide gels, the volume of potential ions per dry gel volume (Z) is related to the degree of hydrolysis of the amide groups to form carboxyl groups. Degree of hydrolysis of amide groups is therefore critical. Degree of ionization (ç) reflects the extent of deprotonation of carboxyl groups and is expected to be pH dependent.

Varying the gel's ionization can be accomplished by adding acid to the initially ionic gel. While a general ionization theory gives clumsy equations (22), two special cases give simple results. First, if the charge in the gel results from ionization of the carboxylic acid groups, then the important equilibrium is

$$K[RCOOH] = [RCOO^-][H^+] \qquad (2)$$

where [RCOOH] and $RCOO^-$ are the concentrations of unionized and ionized carboxylic acid and K is the acid dissociation constant of the polymer. From a mass balance, we expect that

$$[\bar{R}] = [RCOOH] + [RCOO^-] \tag{3}$$

From electroneutrality, we expect that

$$[Na^+] + [H^+] = [RCOO^-] + [A^-] + [OH^-] \tag{4}$$

where $[A^-]$ is proportional to the amount of acid added. Initially, we expect $[Na^+]$ and $[OH^-]$ to be significant; later, as more acid is added, we expect $[Na^+]$ to be diluted by diffusion out of the gel, and $[OH^-]$ to be negligible relative to $[H^+]$. In this limit, we can combine Eqs. (2-4) to find:

$$\xi = \frac{[RCOO^-]}{[\bar{R}]}$$

$$= \frac{[A^-] + K}{[\bar{R}]} \left| \left(1 + \frac{(4K\bar{R})}{([A^-] + K)^2}\right)^{1/2} - 1 \right| \tag{5}$$

When a significant amount of acid has been added, the ionization is small, and this result may be expanded to give

$$\xi = \frac{K}{K + [A^-]} \tag{6}$$

Combining this result with Eq. (1), we find

$$V^{-2/3} = \left(\frac{Z}{kV_{dry}^{2/3}}\right)\left(1 + \frac{[A^-]}{K}\right) \tag{7}$$

Thus a plot of gel volume to the (-2/3) power should vary linearly with the amount of acid added. Such a variation is consistent with the titration of an acid gel with base which was studied earlier (3). Equation (7) was used to correlate test data as described in subsequent chapters.

The development above assumes that the charge on the gel results from ionization of the carboxylic acid, and that this ionization is slight. An alternative approach is based on the assumption that the gel's ionization is governed by ion pairs:

$$K[RCOONa] = [RCOO^-][Na^+] \tag{8}$$

where [RCOONa] is the concentration of ion pairs. Such ion pairs are common in micellar systems, where they obscure about 90% of the potential charge (22). An alternate description of gel volume based on ion pair effects has been described by Andrews (22) and leads to equation (9)

$$V^{2/3} = \left(\frac{ZV_{dry}^{2/3}}{k}\right)\left(1 - \frac{[A^-]}{K}\right) \qquad (9)$$

This model also predicts that gel volume to the (+2/3) power varies with added acid and is essentially the same as equation (7).

It should be noted that the derivation leading to Eq. (7) is approximate in that it does <u>not</u> distinguish between concentrations of small electrolytes inside and outside of the gel. In fact, small electrolyte concentrations may not be equal for three reasons. First, they are influenced by Donnan effects. Second, these concentrations depend on the volume of the surrounding solution. Finally, these concentrations are changed by the changes in the gel volume itself. Gehrke (24,25) has shown that explicit consideration of ion (salt) concentration leads to a different model, described by equation (10).

$$\frac{V}{V_{salt\text{-}free}} = 1 - \frac{2V_{H_2O}}{\frac{\xi V_{dry}}{V_{salt\text{-}free}} - \frac{k}{3}\left(\frac{V_{dry}}{V_{salt\text{-}free}}\right)^{1/3}} \cdot \left\{[A^-]_o - \frac{[RCOO^-]}{2}\left(\sqrt{1 + \frac{4[A^-]_o^2}{[RCOO^-]^2}} - 1\right)\right\} \qquad (10)$$

where $V_{salt\text{-}free}$ is the gel volume without salt. The quantity in braces can be measured independently. Thus a plot of $(V/V_{salt\text{-}free})$ vs. the quantity in braces should be a straight line.

SECTION 5

GEL PREPARATION METHODS AND ANALYTICAL PROCEDURES

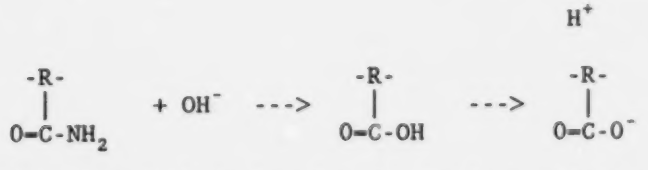
Polyacrylamide gels were prepared from the reagents listed in Table 1. pH sensitive gels were made by polymerizing acrylamide monomer with N,N-methylene-bisacrylamide (MBA) as the crosslinking agent (22). Predetermined amounts of acrylamide and MBA were dissolved in water and the solution was deoxygenated by sparging with nitrogen gas. Ammonium persulfate $(NH_4)_2S_2O_8$ was then added followed by additional sparging. Removal of dissolved oxygen is important because it inhibits polymerization (26). Polymerization reaction is initiated by addition of sodium metabisulfite ($Na_2S_2O_5$). A typical batch procedure involved adding 95 g acrylamide and 5 g MBA to 500 g of distilled water. After bubbling with nitrogen, 5 ml of solution containing 1 g $(NH_4)_2S_2O_2$ and 1.5 g $Na_2S_2O_5$ was added in a 10 second rapid mixing mode. Polymerization was usually completed in a matter of minutes. The gel was then prepared for testing by cutting into small cubes (2-10 mm) and washed with water. Polymerizations were usually carried out at room temperature except when preparing dense polymers which requires use of high concentrations of monomers and result in violent polymerization reactions. For dense polymers temperatures were lowered to 0°C to slow down the reaction. On the other hand, gel preparations with high crosslinker concentrations had to be heated (40°C) in order to increase the solubility of MBA.

Table 3 Reagents for Gel Preparation

Reagent	Grade	Company where purchased
Acrylamide	Baker	J. T. Baker Chemical
N,N'-methylene-bisacrylamide	Practical	Eastman Kodak
N-isopropylacrylamide	Practical	Polysciences
N,N-diethylacrylamide	Practical	Polysciences

Reagents were used with no further purification.

The gels were hydrolyzed in order to prepare pH sensitive gels. As shown below,



The amide group is hydrolyzed under basic conditions to form a carboxyl group. The carboxyl groups are potentially ionizable and give the gel the characteristics of a polyelectrolyte. Hydrolysis was carried out in 0.5 m

solution of sodium carbonate (Na_2CO_3) at 60°C for 24 hours. Gels were then washed and dried.

Temperature sensitive gels were prepared by copolymerization (27). A typical copolymer of Diethylacrylamide and sodium methacrylate was made by using 8 g of N,N-diethylacrylamide , 1.94 cm^3 of a 0.96 M solution of sodium methacrylate, 0.2 g N,N-methylenebisacrylamide, and .02 g of ammonium persulfate in 100 cm^3 of distilled water. The solution was sparged with nitrogen for five minutes to remove molecular oxygen; 0.02 g of sodium metabisulfate was added to catalyze the reaction; the solution was sparged again with N_2, sealed and allowed to react for 20 hours at 6°C (27).

Polyisopropylacrylamide gel was made by dissolving 8 g of N-isopropylacrylamide monomer, 0.1 g of MBA crosslinking agent and 0.005 g ammonium persulfate in 100 cm^3 of water. Dissolved oxygen was removed by sparging with nitrogen before adding .005 g of sodium metabisulfate to initiate polymerization.

Solutions of 25 different chemicals have been tested; they represent a broad range of molecular weights, composition, and ionic character as shown in Table 4. Solutions and suspensions were prepared at several concentration levels; buffer was added and pH adjustment was used with ionic solutes. Feed solutions and raffinates (concentrates), were measured to determine the volumes and chemical concentrations. Distribution of chemicals between the expanded gel phase and raffinate was calculated by material balance. Detailed description of methods and procedures have been presented elsewhere (22,24,27,28); they are summarized below.

Table 4 List of Chemicals Tested

Test Solute	Molecular Weight	Solute Size, nm	Potential Charge	Absorbance
Methyl Orange	327	--	-1	Visible
Bromocresol Green	720	--	-1	Visible
Congo Red	697	--	-2	Visible
Trypan Blue	961	--	-4	Visible
Pentachlorophenol	265	--	-1	UV
2,4-Dichlorophenoxy-acetic acid		--	-1	UV
3,5-Dichlorobenzoate		--	-1	UV
Benzene	--	--	0	
Dinitrobenzene	--	--	0	
Akrazine	--	--	0	
Polyethylene Glycol	400-18,500	--	0	
Polystyrene Latex	--	34.6-990	0	
Polyethylene Oxide	600,000	--	0	
Hemoglobin	64,500	6.2		
Ovalbumin	45,000	--		
Gelatin				
Vitamin B12	1,355	--	0	Visible
Sucrose	342	.8	0	--
Urea	60	.5	0	--
Propanol	--	--	0	--
Isopropanol	--	--	0	--
Tertiary Butanol	--	--	0	--
Silica	--	5	0	--
Zn	--	--		--
EDTA	--	--		--

A Perkin Elmer Model 139 and a Beckeman 26 UV-vis Spectrophotometer was used to measure solution concentrations of Vitamin B12, Blue Detran, and pentochlorophenol. Polyethylene glycol, polyethylene oxide and ovalbumin suspension were measured by refractommetry using a Brice Phoenix differential refractometer. Suspension of polystyrene and gelatin were analyzed by weighing the residue after evaporating to dryness.

Vitamin B12 solutions were tested because it is an uncharged, intermediate size molecule, with a molecular weight of 1355 g/mole; it consists of a corrin ring coordinated to a central cobalt atom that gives it a relatively stable structure; it is highly colored so that even dilute solutions (10^{-5} molar) can be measured photometrically at a wavelength of 550 nm; a typical calibration curve is shown in Figure 4. In order to minimize errors, samples were diluted to give absorbance readings around 0.40 units (approximately 10^{-5} molar). Beer's law applies in this region as shown by the linear correlations between concentration and absorbance.

Solutions of methyl orange and bromocresol green, were tested because they are monovalent solutes, in the medium molecular weight range, and easily measured spectrophotometrically in the visible spectral range using the same procedure described for Vitamin B12.

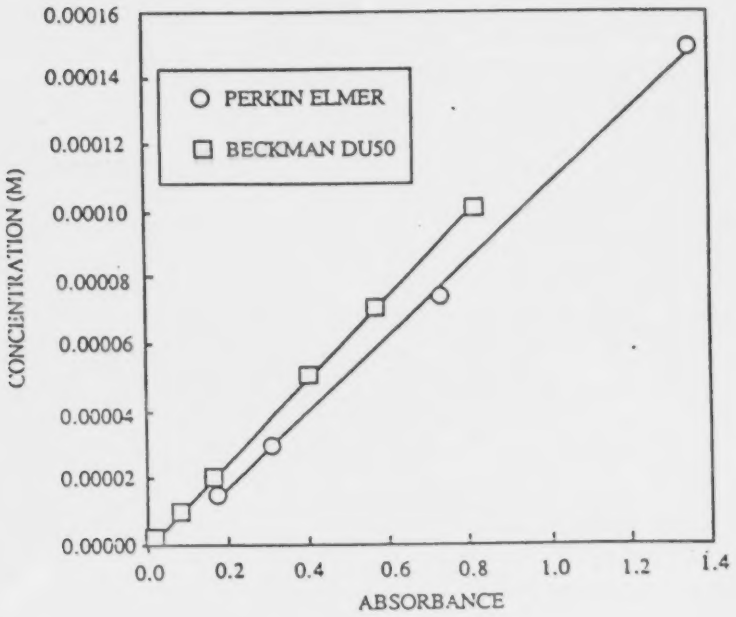


Figure 4 : Graph of concentration vs. absorbance for vitamin B_{12}.

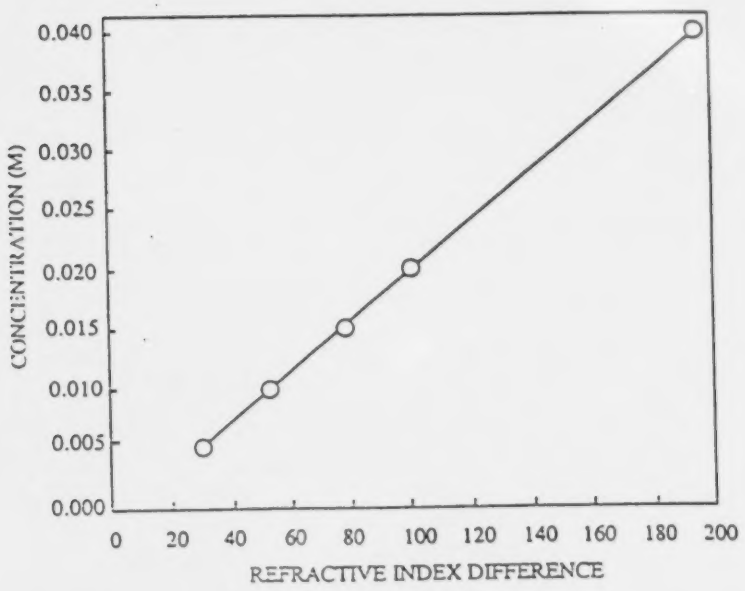


Figure 5 : Graph of concentraion. vs. refractive index difference for PEG 400.

Solutions of Congo Red and Trypan Blue are multivalent solutes, medium molecular weight range and easily measured spectrophotometrically in the visible range.

Polyethylene glycol (PEG) suspensions were tested because it is nonionic and molecular size graded materials covering a broad range of molecular weights are available commercially from Aldrich. PEG concentrations were measured using a Brice Phoenix Differential Refractometer to measure the difference in refractive index resulting from addition of solute. Typical calibration curves for PEG, nominal molecular weights of 400 and 3400 g/mole respectively are shown in Figure 5 and Figure 6; refractive index and concentration are linearly related. Calibration curves were therefore used to calculate sample concentrations from refractive index measurements.

Polyethylene oxide and ovalbumin suspensions were analyzed by measuring refractive index and comparing with calibration curves in the same manner as described above.

UV absorbance was used to measure concentrations of pentachlorophenol (258 nm), 2,4-dichlorophenoxyacetate (282 nm), and 3,5-dichlorobenzoate (283 nm).

Zinc and EDTA-Zn complexes were measured by atomic absorption using a Varian Atomic Absorption Spectrophotometer (AA-175 Series). Benzene, dinitrobenzene, propanol, isopropanol, tertiary butanol, and atrazine concentrations were calculated from measurements of dissolved organic carbon (DOC). DOC was measured using a Beckman 915A TOC analyzer.

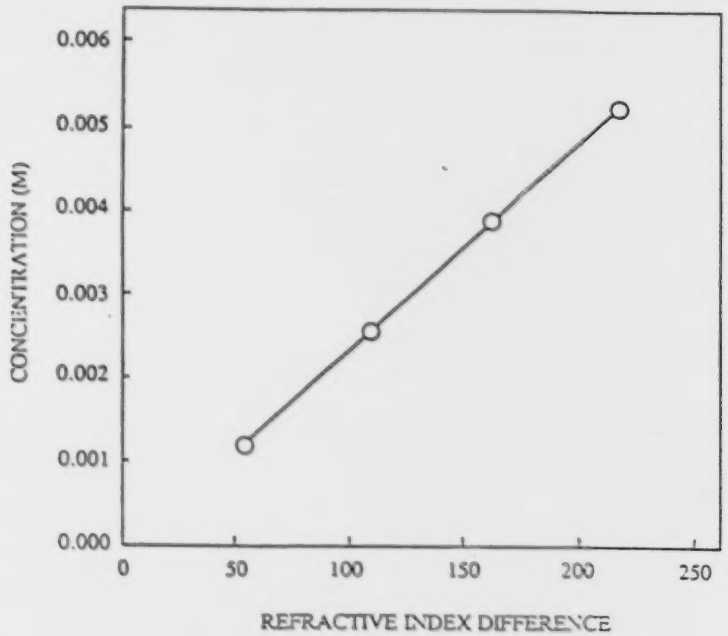


Figure 6 : Graph of concentration. vs refractive index difference for PEG 3400.

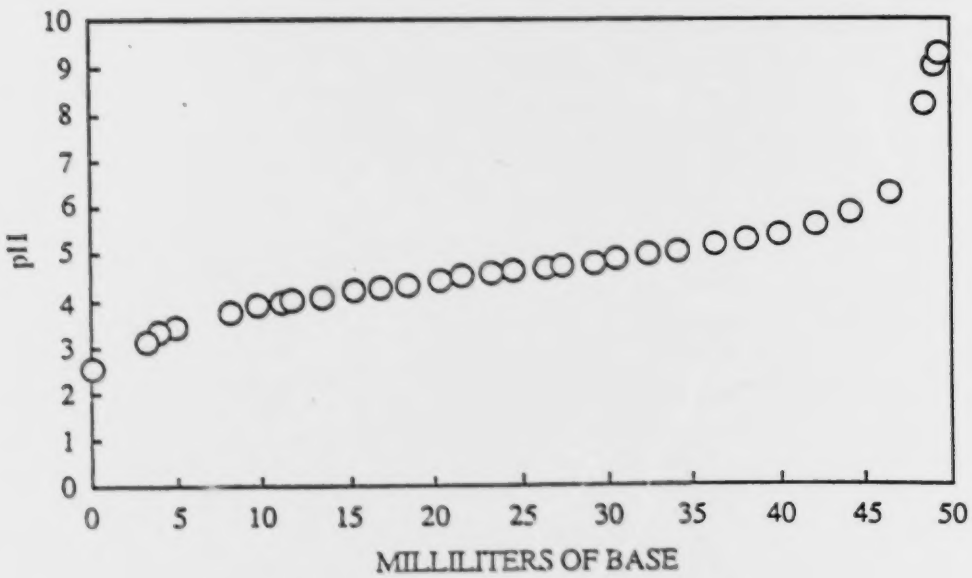


Figure 7 : Titration of linear polyacrylic acid

SECTION 6

STUDIES OF GEL VOLUME

Potentiometric Titration of Gel Phase

A series of acid-base titrations were carried out to measure the ionization capacity of gels and to establish the effects of changing pH environment on gel volume. The effect of pH changes on gel volume is important because it is the driving force for expanding and contracting the gel. Ionization is the underlying chemical mechanism that causes gel expansion and thus actuates the intake and expulsion of water.

Two aspects were investigated. Acid-base neutralizing capacity of gels was measured as a function of pH by titrating in a carbon dioxide free atmosphere. The objective was to determine the potential ionizing capacity (Z) of the gel. A related series of experiments was designed to measure gel volume at different pH levels to quantify capacity for uptake and release of water.

pK Values of Hydrolyzed Gels

Preweighed amounts of dry gel were contacted with distilled water and allowed to equilibrate and swell completely. The initial pH of the resulting water phase was usually in the 8-9 pH range. As indicated in the section on gel preparation, the dry gel was in the sodium form. Dry gel was prepared by repeated washing of the sodium carbonate hydrolyzed gel before drying in an oven at 70°C.

Aliqots of expanded gels were titrated with acid (0.1 or 0.01 M HCl). Small amounts of acid were added, and pH was allowed to stabilize. This sequence was repeated over a broad pH range until the gel was completely collapsed. pH was measured using a Coleman Model 39 Analyzer and standardized using purchased standards.

Test results on a solution of uncrosslinked linear polyacrylic acid are shown in Figure 7. The titration curve relates pH to milliliters of equivalent base neutralized by acid addition. The inflection point indicates that pK (acid dissociation constant) is approximately 4.77. However, it is evident that the titration curve extends over a broad pH range, which suggests that pK is not a unique constant. Mandel (29) has shown that this is indeed the case for polyacrylic acids. Figure 8 shows that pK values increase with increasing degree of dissociation. The presence of salt, eg. $NaNO_3$ or NaCl, lowers the calculated pK values significantly and also reduces the effect of α on pKa. Mandel (29) showed that the changes in pK as a function of degree of dissociation (ξ) can be represented by a second degree polynomial

$$pK = pKo + \Phi_1(\xi) + \Phi_2\xi^2$$

Values of Φ_1 and Φ_2 are approximately 4.0 and -1.7 respectively for low salt concentration environments. With increasing salt concentrations, there is a progressive decrease in Φ_1 and a progressive increase in Φ_2.

With reference to equation (1), changes in pK do not affect the potential ion concentration (Z) for a completely ionized polyacrylamide gel

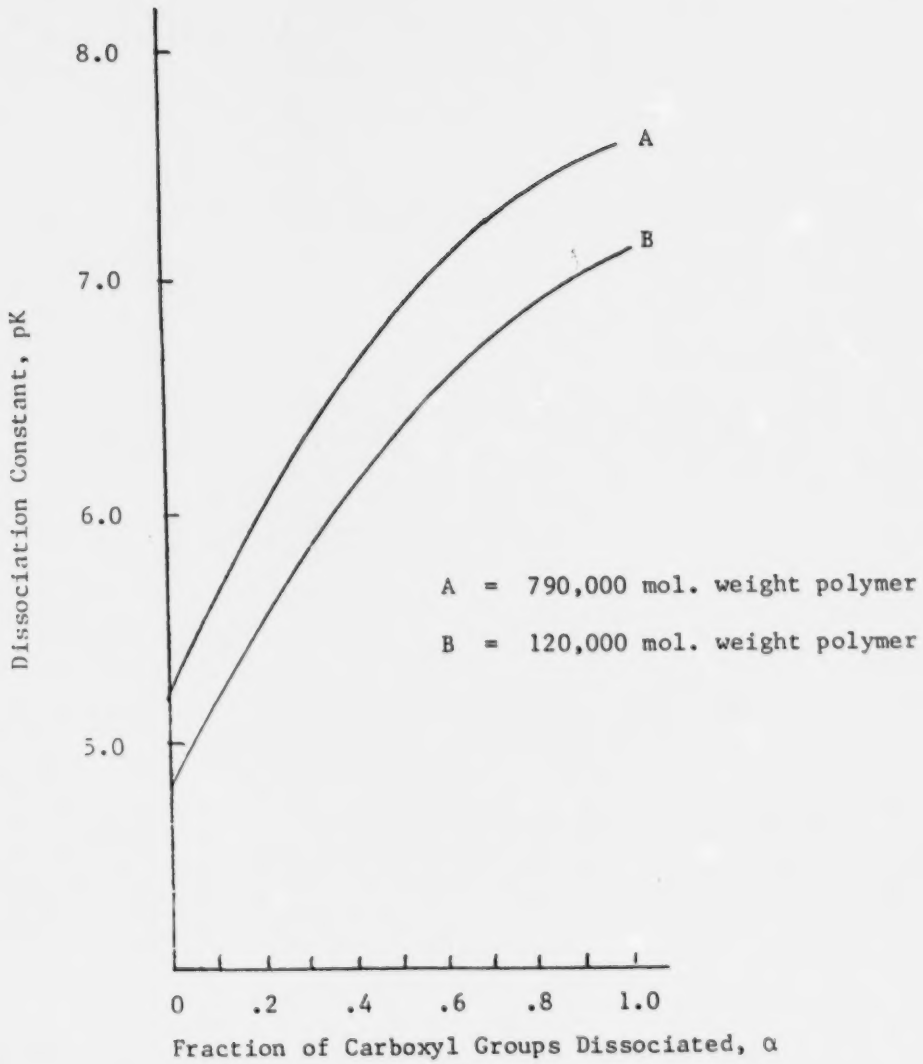


Figure 8 pK Values as a Function of Degree of Dissociation of Polyacrylic Acid Polymer (After Mandel, 1970)

but will affect ξ the fraction of sites ionized at a given pH and thus influence the gel's swelling behavior as a function of pH. From a mechanistic viewpoint, the change in pK with pH indicates that gels are not chemically homogenous. Some carboxyl groups are more easily ionized whereas other groups are in effect shielded.

Effect of pH

Gel phase swelling and contraction ratios are important because they determine the volume of water that can be extracted and removed from feed solution. Theory predicts that expansion is affected by the gel's physical-structural properties as well as solution chemistry. Equation (1) shows that gel elasticity (K) and concentration of potentially ionizable groups (Z) are major variables. Solution properties, eg. pH, which in turn affect the degree of ionization (ξ) are equally important as discussed above. Elasticity and concentration of potentially ionizable groups can be modified by changing the degree of crosslinking and acrylamide concentrations (22).

Polyacrylamide gels with different swelling potentials were therefore prepared by varying acrylamide concentration and by varying crosslinker concentration (MBA) as shown in Table 5. Increasing acrylamide concentration in the original water solution produces a denser polymer whereas increasing crosslinker concentration produces a more constricted three dimensional framework.

Water uptake of the gels in Table 5 were measured over the pH range from 2 to 10. Dry gel (0.1 - 0.5 g) was immersed in distilled water and allowed to equilibrate after each stepwise addition of HCl. Gel volume and solution pH were measured after each step. The results are summarized in Figure 9, in terms of the ratio of gel volume (V) to dry weight of gel (M_d) as a function of pH. Gel volume (V) is sufficiently large so that its specific gravity is approximately equal to that of water. Therefore V/M_d is equivalent to the weight ratio of wet to dry gel. As shown in Figure 9, all gels expand with increasing pH. Maximum expansion ratio for 2% crosslinked gel was 130^+; gels with 15-20% crosslinker have lower ratios, in the range of 10 - 15. However, gels made with high crosslinker concentration have higher physical rigidity and can be handled more easily. They are probably more durable in repeated cyclic usage. The tradeoff between larger expansion ratio and ease of handling or durability was not fully investigated in this study but should be considered in future studies and development of the gel extraction process.

Theoretical consideration of the swelling behavior of gels in response to acid base titration suggest that the ratio $(V/M_d)^{-2/3}$ varies linearly with the amount of acid added, as shown by equation (1). Figure 10 shows that the data obtained with highly crosslinked gels can be correlated using equation (7). However, the titration-volume data for low crosslinker concentration gels are not linear. It should be noted that the derivation of equation (7) invokes several simplifying assumptions that have been discussed elsewhere (22,24,28) and will not be elaborated on in this report.

The assumption that pK is constant is probably not valid over the whole titration range as pointed out in the previous section. Another shortcoming of the simplified model embodied in equation (7) is that gel particles are assumed to be homogeneous with regard to the hydrolysis of acid groups which in turn determines the spatial distribution of ionizable sites. Studies of the effects of gel particle size and configuration are needed to assess this question.

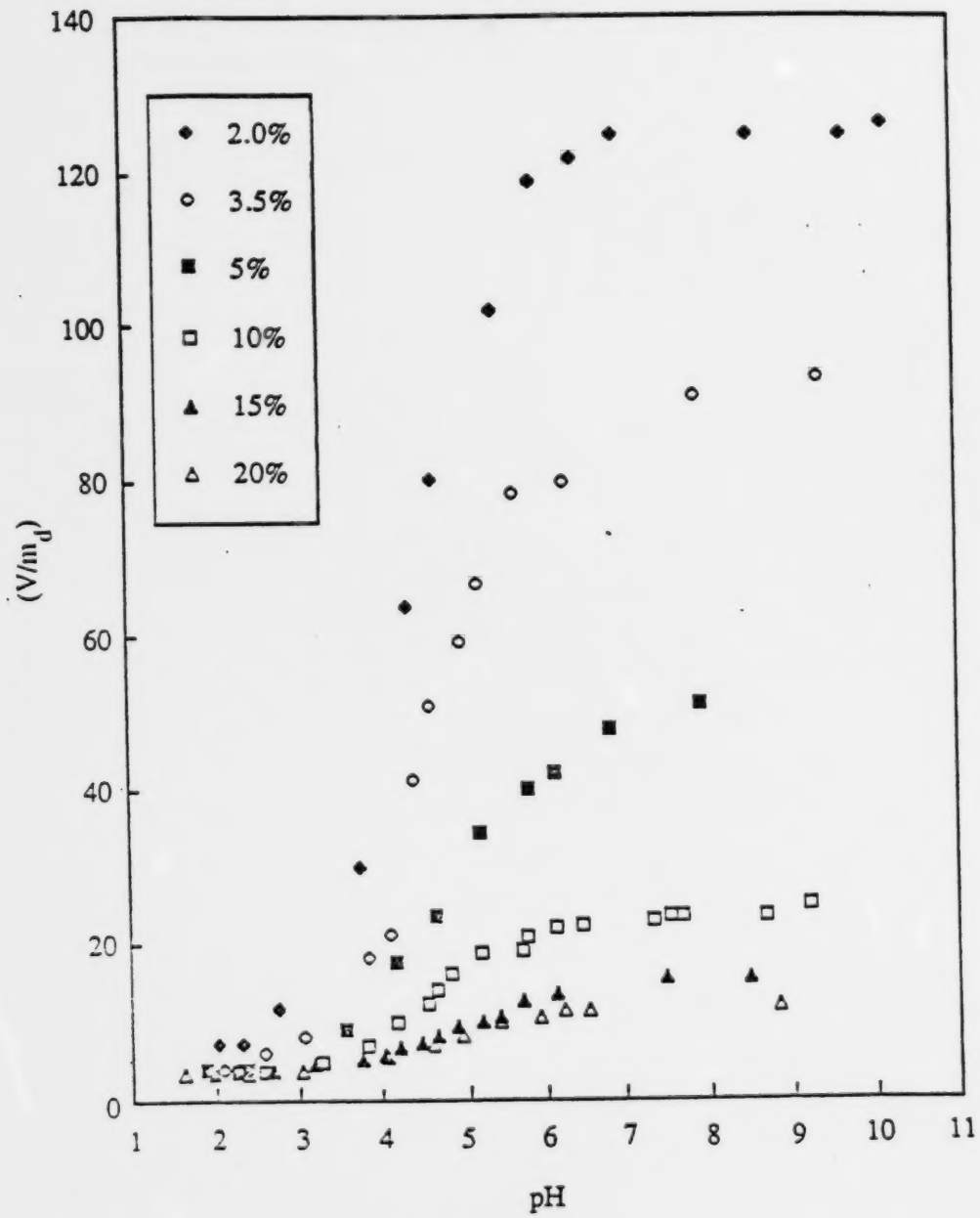


Figure 9 : Gel volume as a function of solution pH.

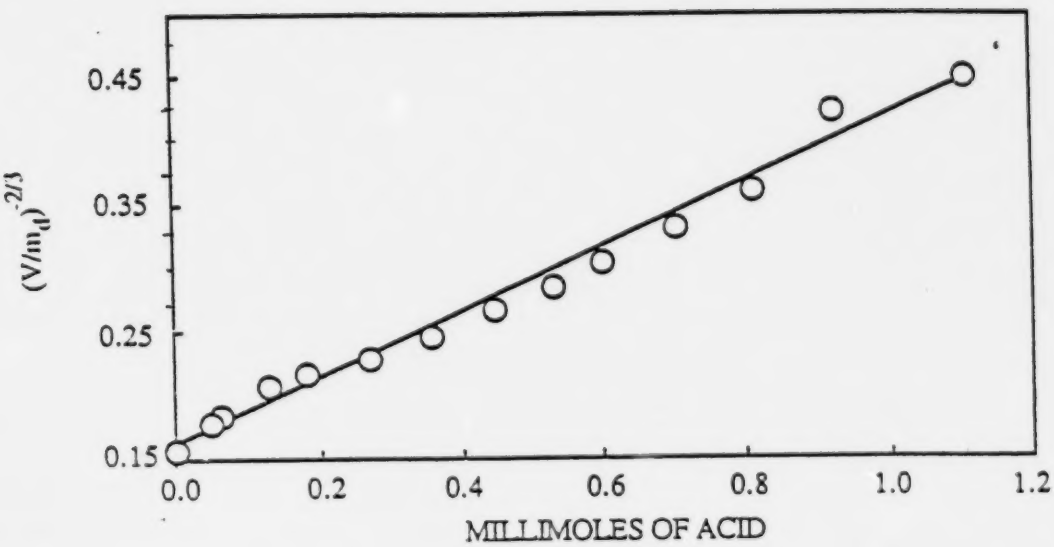


Figure 10 Acid Titration of Gel

Table 5

Physical Chemical Composition of Gels

Wt of Ac	Wt of MBA	Vol of Water	x-link fract.	Acryl conc
4.902 g	0.100 g	15.0 ml	0.020	0.333 g/ml
4.900 g	0.100 g	25.0 ml	0.020	0.200 g/ml
4.903 g	0.100 g	45.0 ml	0.020	0.111 g/ml
4.826 g	0.176 g	15.0 ml	0.035	0.333 g/ml
4.827 g	0.177 g	25.0 ml	0.035	0.200 g/ml
4.825 g	0.174 g	45.0 ml	0.035	0.111 g/ml
4.749 g	0.251 g	15.0 ml	0.050	0.333 g/ml
4.750 g	0.251 g	25.0 ml	0.050	0.200 g/ml
4.749 g	0.249 g	45.0 ml	0.050	0.111 g/ml
4.499 g	0.500 g	15.0 ml	0.100	0.333 g/ml
4.502 g	0.501 g	25.0 ml	0.100	0.200 g/ml
4.500 g	0.500 g	45.0 ml	0.100	0.111 g/ml
4.251 g	0.752 g	25.0 ml	0.150	0.200 g/ml
4.000 g	1.000 g	25.0 ml	0.200	0.200 g/ml

Maximum Gel Expansion

For practical applications, the gel's maximum expansion capacity is more important than its pH volume response. As shown in Figure 9, gel expansion rations are at a maximum and appear to level off at pH 8. Volume contractions have been observed at higher pH levels. With reference to equation 1, maximum expansion is expected to occur at ξ =1.0, when all potential sites are ionized. This effect of pH on gel expansion is consistent with the data of Mandel (29) showing that pK values for completely ionized polyacrylamide gels are in the range of 4.5 to 7.5.

The simplified theory of gel expansion incorporated into equation 1 predicts that ultimate expansion ratio $(V/m_d)^{-2/3}$ is directly proportional to elasticity (K) and varies inversely with concentration of ionic sites (ξZ). Since elasticity is defined in terms of the effective number of polymer chains in the network, it can be assumed that expansion ratio is related to crosslinker concentration. On the other hand, changing the acrylamide concentration and the degree of hydrolysis of amine groups is expected to affect the concentration of potentially ionizable groups (Z) so that the expansion ratio is also related to acrylamide concentrations and degree of hydrolysis. To test these interpretations, maximum expansion ratios (at pH>9) were correlated with crosslinker concentrations and the product of crosslinker and acrylamide concentrations. Figure 11 shows that volume ratios are linearly related to the concentration of crosslinker. This is in accord with the theoretical model considerations incorporated into equation (1). Figure 12 shows that volume ratio also varies linearly with the product so that gel volume characteristics can be related to gel formulation as predicted by equation (1). As shown in the insert,

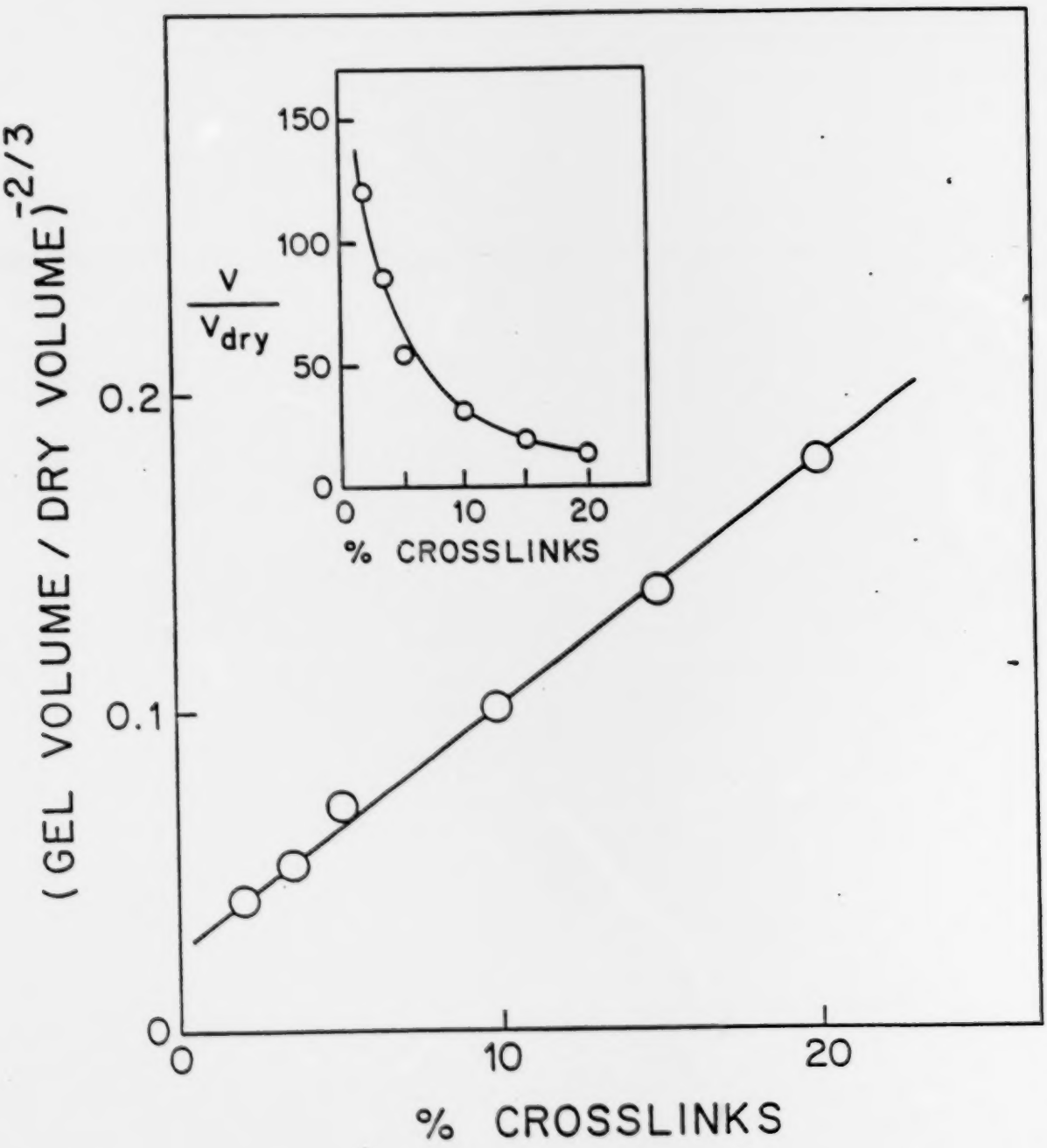


Figure 11 Gel Swelling Decreases with Increased Crosslinking.

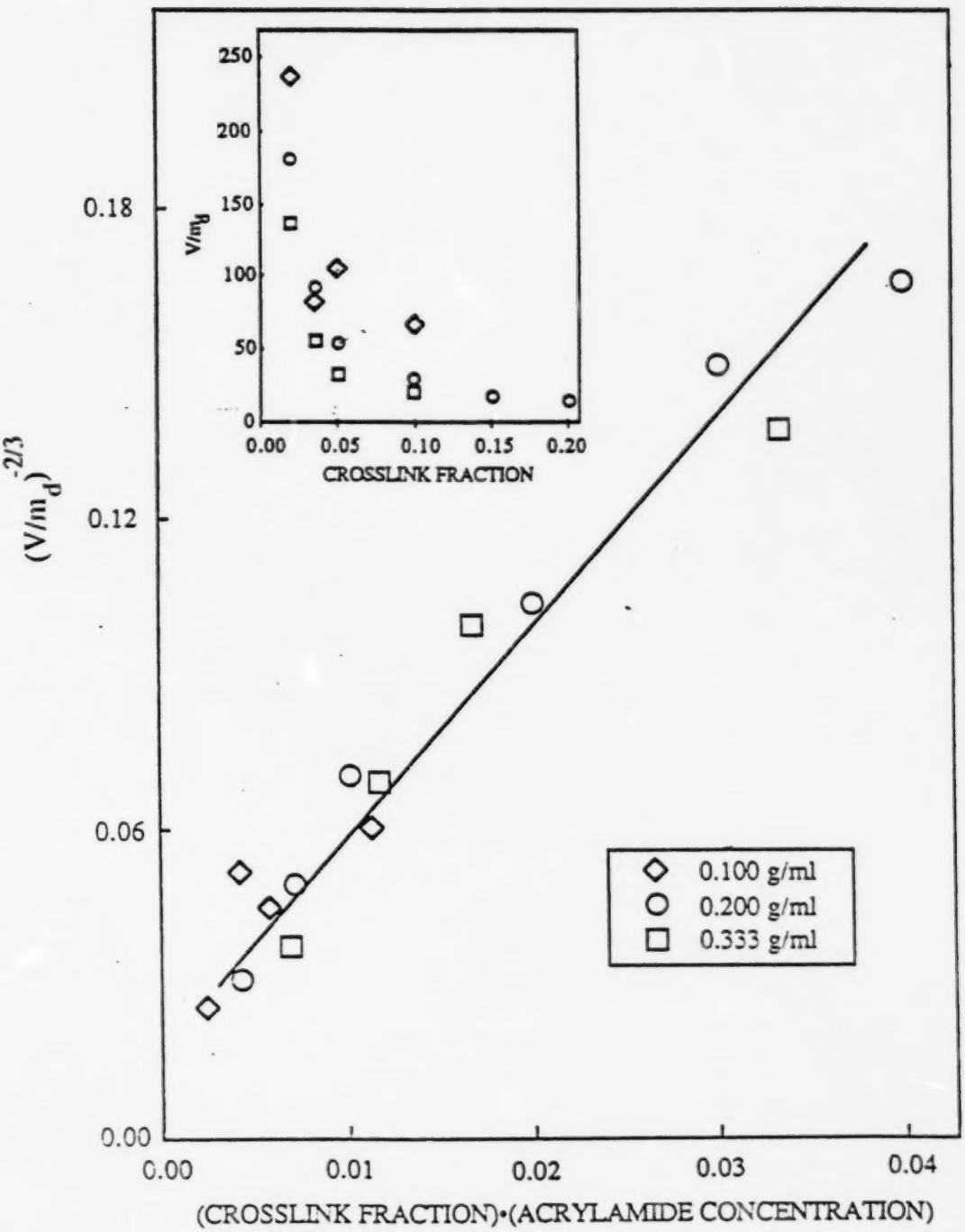


Figure 12 Swelling data showing the volume to the (-2/3) as a function of the crosslink fraction and acrylamide concentration.

increasing crosslinker concentration results in smaller expansion ratios. Increasing acrylamide concentration which produces a denser polymer also reduces expansion ratios.

Analysis of Volume-pH Relationship

The objective of these experiments was to characterize gel performance starting with collapsed gels that had been pretreated with HCl to simulate acid regeneration. Measurements were made to provide information on gel volume as a function of pH, rejection efficiency for pentachlorophenol, and acid-base requirements for collapsing and expanding the gel.

Aliquots of oven dried gel PAC-1 (0.06 grams) were contacted with 10 ml of acidified water, HCL solutions ranging from 0.004 to 0.08 HCl, and allowed to equilibrate on a shaker; the measured values of gel mass and pH after equilibration with acid are listed in Table 6. Solution pH increased in all cases due to the alkalinity associated with the dry gel. PAC-1 gel had been dried after hydrolysis and washing and it contained a small amount of residual base (1.6 wt% NaOH) in addition to the alkalinity associated with ionized acrylic acid groups.

Table 6

Preparation of Acidified Gels

Experiment No.	Dry Mass g	Acidified Water pH	Solution-(1) mass,g	Equilibrated (2) Raffinate pH	Gel Mass,g
38.1	.060 g	1.33	10	1.37	1.300
38.2	.060 g	1.37	10	1.46	1.320
38.3	.060 g	1.48	10	1.7	1.180
38.4	.060 g	2.03	10	4.44	2.660
38.5	.060 g	2.16	10	5.02	4.340
38.6	.060 g	2.27	10	5.91	6.800
38.7	.060 g	2.45	10	6.3	7.150

(1) HCl solutions added to dry gel.
(2) Measured after equilibration; raffinate was removed by filtration.

Acidified gels were contacted with 20 ml of 50 mg/l PCP solution (pH = 11) and again allowed to expand by equilibrating on a shaker. Raffinate was removed by filtration and measured. Raffinate concentrations of H^+ and OH^- were calculated from pH measurements. PCP concentrations were measured by UV absorbance. Results are shown in Table 7.

As shown in Figure 13, gel mass is related to residual pH; the gel imbibed a small amount of water (1.3 g) at low pH; more swelling was observed above pH 4. At pH 6.3, wet gel mass is 7.1 g or 120 fold larger than the dry gel. Additional swelling was observed after pH was increased due to exposure to 20 ml of basic PCP solution (pH 11). As shown in Table 7 and Figure 13, gel mass increased to 10-11 g at pH 7-8.

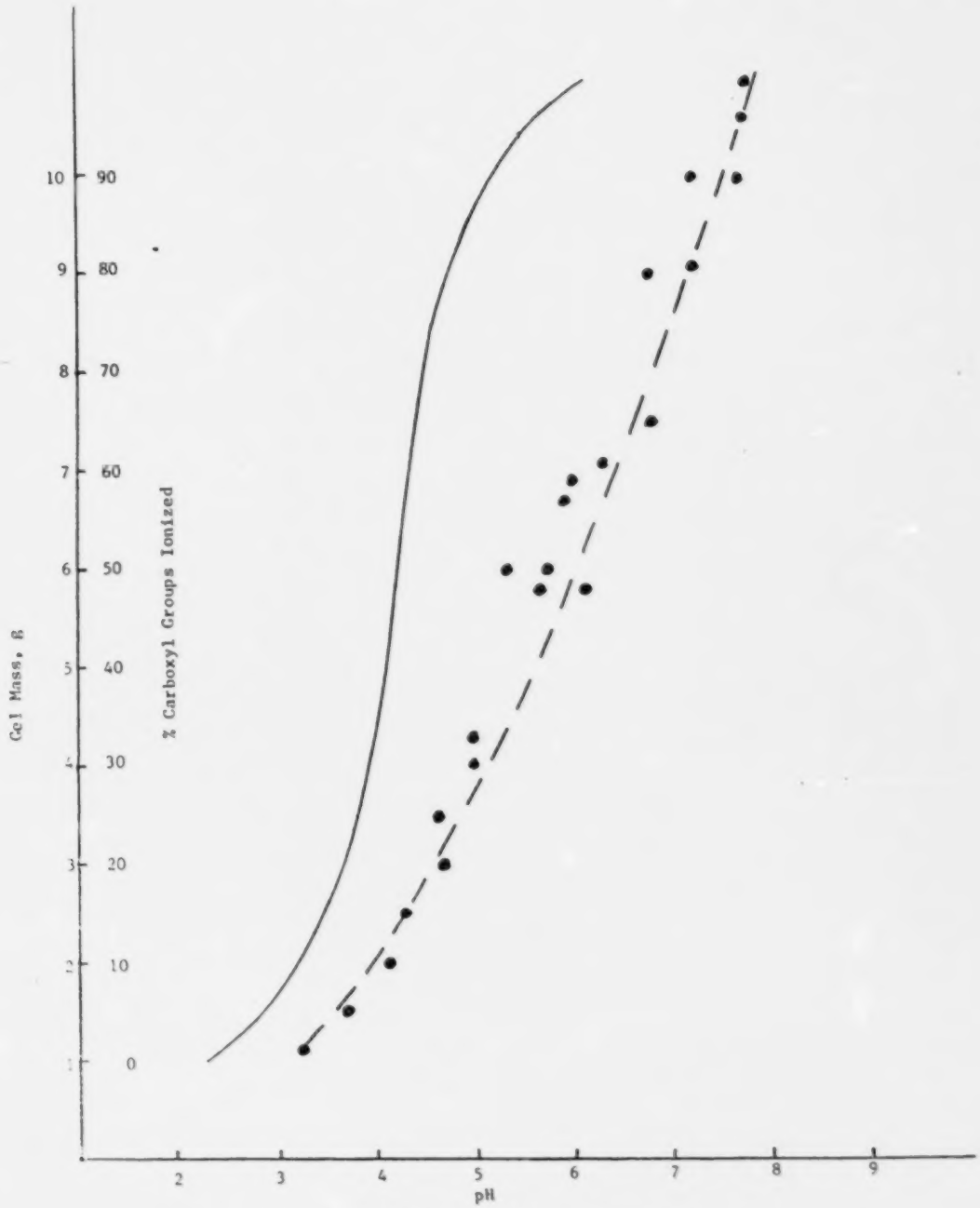
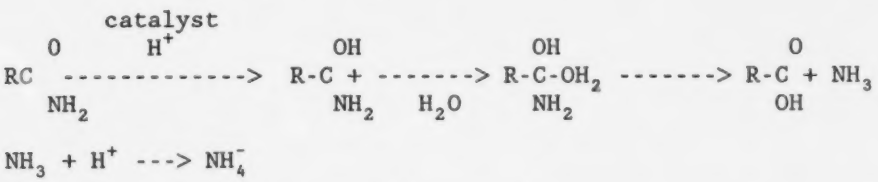


Figure 13 Gel Volume Versus pH of Solution Being Extracted

Quantities of acid and base added with the feed solution and with the original gel were analyzed in order to calculate the moles of acid needed to expand the gel from its collapsed form at low pH to its expanded state at high pH. Mole ratios of hydrogen ions per mole of gel (H^+/gel) were calculated for each test. The ratios represent the moles of H^+ absorbed and/or neutralized by the gel after correcting for pH related changes in H^+ concentration. As shown in Figure 14, the ratio increases linearly with decreasing pH except at low pH values. The corresponding gel mass data show the expected trend, gel volume increases as a function of pH; the largest changes occur at pH>4 which corresponds to the pK range of acrylic acid polymers. The apparent consumption of H^+ ions at low pH is not related to any changes in gel volume. Furthermore, the pK values of acrylic acid polymers suggest that carboxylic acid groups are protonated at pH>2.

The most likely explanation for the continued uptake of H^+ ions by the gel is that amide groups are hydrolyzed at low pH conditions. Acid hydrolysis of amides by nucleophilic substitution is postulated (30)



$$NH_3 + H^+ \text{ ---> } NH_4^-$$

Hydrolysis consumes one atom of H^+ per amide group hydrolyzed. It therefore appears that the strongly acidified gels (Experiments 38.1-2-3) underwent additional hydrolysis to the extent of 0.4, 0.25, and 0.17 moles/mole respectively.

The permanent disappearance of H^+ in part A of experiments 38.1-2-3 was confirmed in part B of the test when basic pentachlorophenol was added. Material balance on H^+ and OH^- confirmed that H^+ had been neutralized by the gel.

Hydrolysis of amide groups is a potential variable that needs to be considered in developing regenerating procedures. pH should be maintained above 2 to avoid changes in the gel's chemical structure. Another alternative is to use completely hydrolyzed gel, e.g. polyacrylic acid.

Effects of Dissociation Constant

As discussed in a previous section, pK of weak polyacids is not a unique constant; degree of dissociation (ς) and salt concentration (μ) have significant effects (29).

pK of acrylic acid is 4.26 at 25°C and if pK were constant, there should be less than 5% ionized groups at pH 3 and more than 95% ionized at pH 5.2 as illustrated in Figure 13. Since gel expansion is related to ionization, expansions should occur in the pH range 3 to 5.2. Figure 13 shows that the measured increase in gel volume occurred over a broader pH range (3 to 7.5). One possible explanation is that pK increases with increasing ξ. As discussed in a previous section, Mandel (29) has shown that the pK of linear polyacrylamides can be described by a second degree polynomial in ς. However, the partially hydrolyzed crosslinked polyacrylamide gels (PAC-1) used in the present studies are significantly different from linear PAA. On the one hand, PAC-1 is partly hydrolyzed so

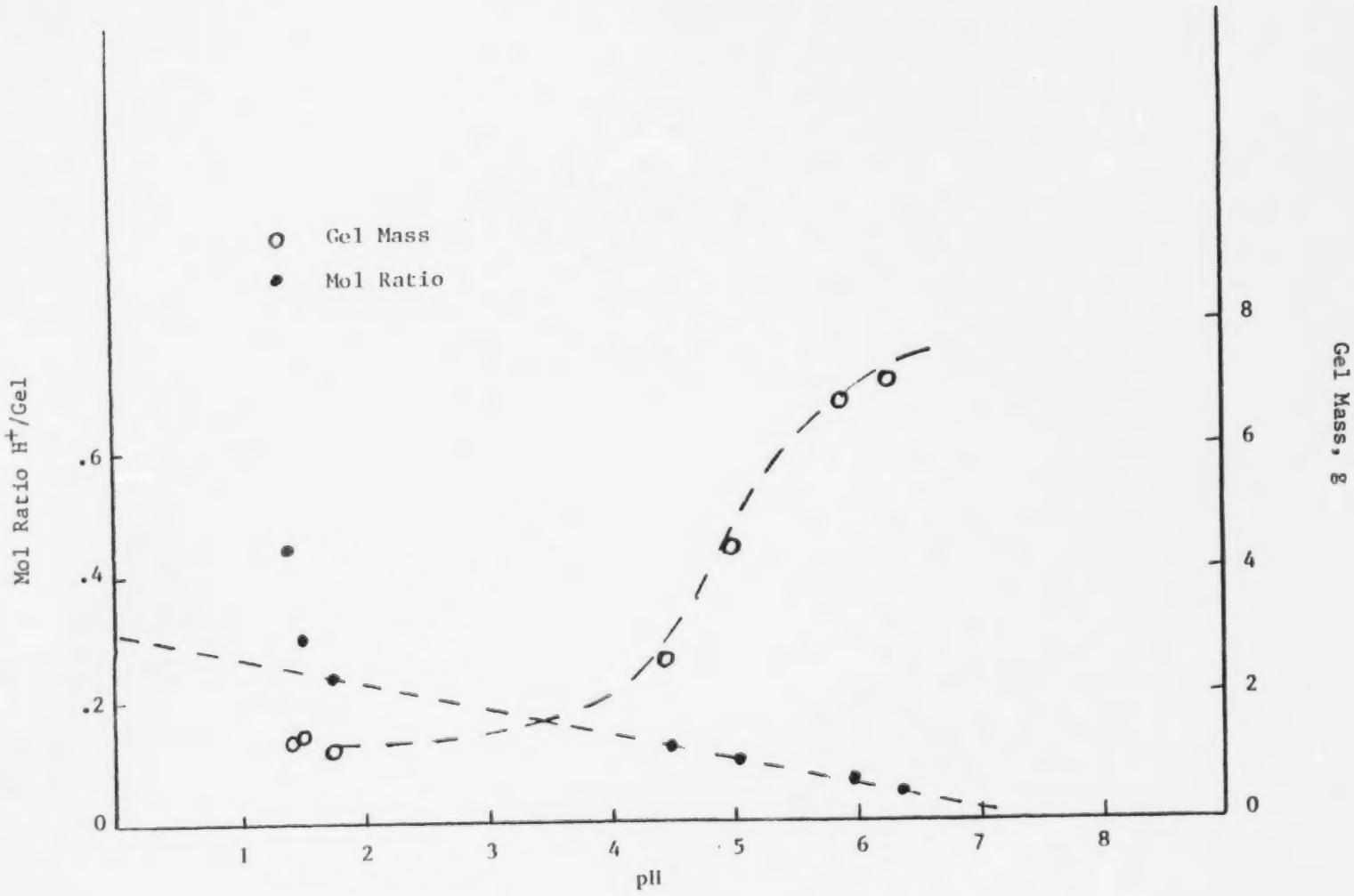


Figure 14 Mol Ratio of Hydrogen Ions to Gel

Table 7 Extraction of PCP Solution Using Acidified Gels

Expmt #	Pentachlorophenol Feed Solution: Nominal Conc (ppm)	Measured Conc(ppm)	pH(1)	Mass(g)	Raffinate: Mass(g)	PCP Conc(ppm)	pH	Gel Phase (2): Mass(g)	Calculated Rejection Efficiency
38.7	55	56.5	11.0	20.0	15.4	35.5	3.1	5.90	124%
38.2	55	56.5	11.0	20.0	15.4	29.0	5.7	5.92	163%
38.3	55	56.5	11.0	20.0	14.2	43.0	6.0	6.98	58%
38.4	55	56.5	10.9	20.0	15.0	63.3	6.8	7.66	36%
38.5	55	56.5	10.9	20.0	15.2	63.3	7.1	9.14	38%
38.6	55	56.5	10.9	20.0	16.0	61.8	7.4	10.80	38%
38.7	55	56.5	10.9	20.0	17.1	58.8	7.7	10.05	16%

(1) Nominal concentration of NaOH used in preparing PCP solution, moles/l.

(2) Initial conditions of gel phase are shown in Table 4.

that the number of potentially ionizable groups is significantly lower than PAA. However, the proximity of carboxyl groups is significantly greater in the PAC-1 gel because the strands are crosslinked. Volumes per unit of ionizable group were calculated for PAA and PAC-1.

The volume of a single chain of PAA was approximated as the cylindrical volume of influence of a linear chain of molecules; the radius r was taken to be the same as the length of one unit of acrylic acid. Crosslinked polymer was assumed to be a cubical arrangement of parallel chains that are held in place by crosslinks. The calculations show that the volume per acrylamide for a gel structure with a very large number of chains is reduced by a factor of 4. Interactions between adjacent groups are therefore increased. As a first approximation, this volume reduction was assumed to be equivalent to a four fold larger concentration of potentially ionizable groups. The effective degree of dissociation (ξ') of PAC-1 gel at a fixed pK was therefore defined by

$$\xi' = \xi \ (R_T \ / \ R_H \times 4) \qquad (11)$$

where R_T is the total monomer concentration, R_H is the concentration of hydrolyzed monomers, and ξ is the degree of dissociation. R_T/R_H is the fraction of amide groups hydrolyzed and therefore a measure of the potentially ionizable groups. pK values were calculated using the polynomial for PAA at a salt concentration of 3.3×10^{-3} moles/l.

$$pK = 4.94 + 3.5\xi - 1.1\xi^2$$

The percent of ionized carboxyl groups ($RCOO^-/R_H \times 100\%$) as a function of pH was calculated for three cases representing progressively greater hydrolysis. Case A is based on 5% potentially ionizable groups ($R_H = 0.05\ R_T$); case B is based on 12.3% potentially ionizable groups, and case C is for a completely hydrolyzed gel ($R_H = R_T$). Case B is representative of the degree of PAC-1 hydrolysis estimated from the H^+ utilization calculations described for Experiments 38.1-7 in previous paragraphs.

The results are shown in Figure 15. The slope of $\%RCOO^-$ versus pH correlation lines decrease with increasing RH (Concentration of potentially ionizable groups). It is interesting to note that the pH range for case B is essentially the same as the gel mass versus pH correlation of the data from tests 38.1-7. The similarity between the correlation lines for gel volume versus pH and $\%RCOO^-$ versus pH indicates that variable pK is likely to give a better prediction of volume changes than a constant pK value. As shown in Figure 15, constant pK values predict a rapid change in $\%RCOO^-$ versus pH; furthermore the change occurs at lower pH than the observed volume changes.

Extrapolation of the correlation suggests that:

a) increasing the concentration of potentially hydrolyzable groups broadens the pH range for complete expansion of the gel;
b) increasing salt concentration of the medium decreases pK values as well as the effect of ξ on pK.

For practical applications, narrowing the pH range in which gel volumes expand or contract is desirable because it reduces acid-base requirements. However, the amount of titrant needed to neutralize or ionize the carboxyl groups is usually much larger than the titrant needed to change solution pH in the 4-8 range so that the savings in titrant are likely to be small.

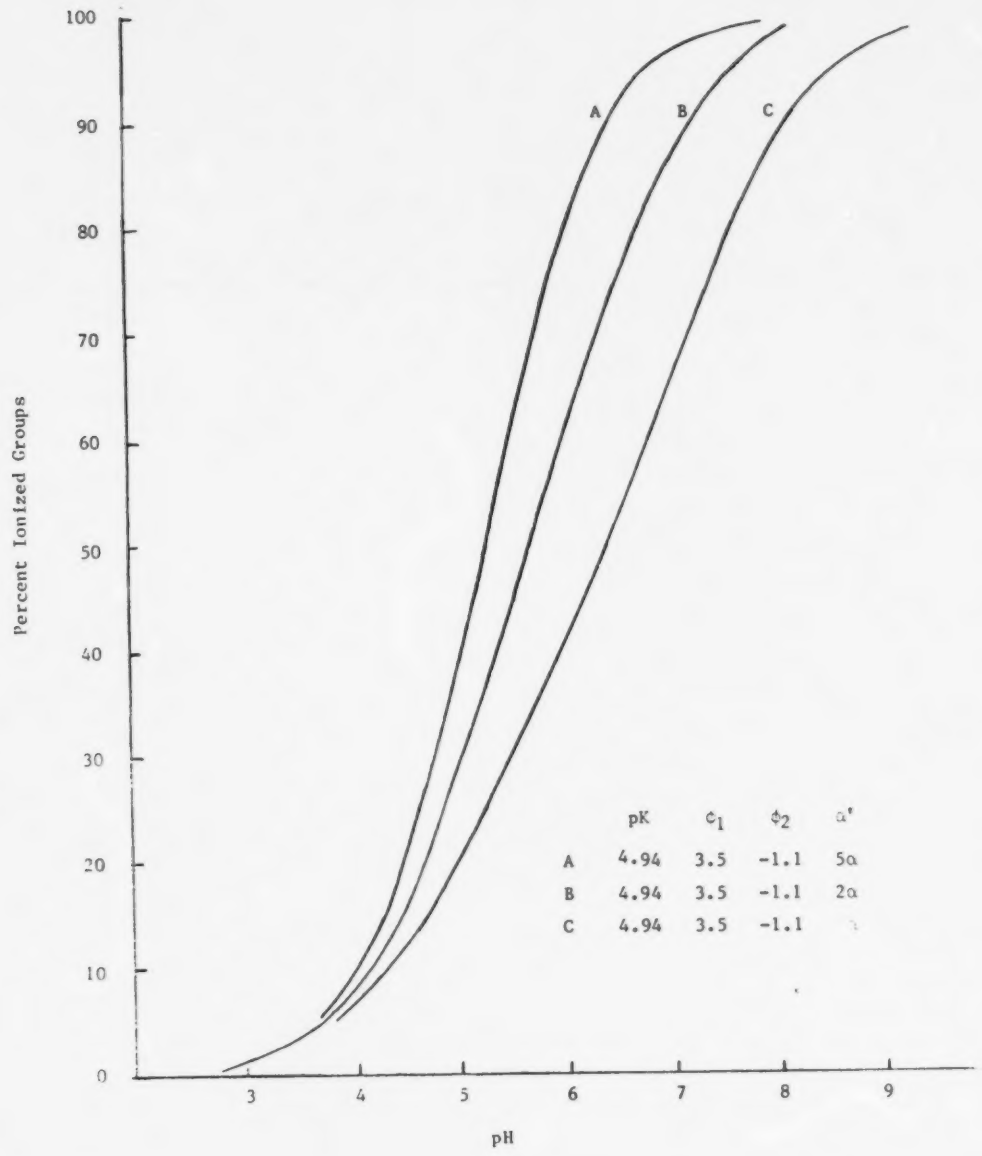


Figure 15 Effect of pH on Ionization of Carboxyl Groups

A major disadvantage for using high salt concentration media is that it shifts the volume expansion/collapse curve to lower pH ranges. This could interfere with separation of weak acids because they require high pH conditions to induce ionization. This will be discussed in more detail in a later section.

Effect of Salt Concentration

Theoretical aspects of the effects of salt concentration on gel expansion have been discussed in a previous section. Equation 10 relates gel volume in the presence of salt relation to the volume in salt free solution based on considerations of ion distribution inside and outside the gel. In effect, this implies that gel expansion is affected by osmotic pressure differences (25,29).

A series of tests to measure salt effects were carried out using well washed samples of acidified gel. The collapsed gels were added to appropriate solutions of alkali metal hydroxides and allowed to swell. All of these gels were swollen by the same amount, whether the counterion was lithium, sodium or potassium. The gels were then titrated with the corresponding alkali metal chloride, i.e. the lithium gel was titrated with lithium chloride, etc.

The gel's swelling decreases with the addition of salt, as shown in Fig. 16. The swelling is reduced by the same amount for each salt used, suggesting that the effect is osmotic and electrostatic, rather than the result of specific chemical interactions. It is postulated that Donnan equilibrium excludes salts from the gel and reduces the activity of the water in the surrounding solution. Accordingly gel volume is a function of added salt, a result summarized by Eq. (10). The quantity in braces in Eq. (10) is a measure of the osmotic force which is known experimentally, and which is that shown on the abscissa of this figure. The linear variation of the volume with the osmotic force supports the interpretation that gel swelling in salt solutions is controlled by Donnan equilibria.

Temperature Sensitive Gels

The findings that modified polyacrylamide gels exhibit abrupt changes in volume in response to small changes in temperature has important practical implications (27,31). It has been demonstrated that the gels expand by imbibing water at low temperature and reversibly collapse by expelling water at a slightly higher temperature. This phenomenon has been ascribed to the fact that the polymer is near its lower critical solution temperature. The volume changes are therefore closely related to the polymer's chemical composition and chemical activity vis a vis that of the surrounding solution.

A series of tests were carried out to characterize the volume - temperature behavior of selected gels that were prepared for this purpose. Gel preparation has been described in a previous section. Aliquots of dry gel (0.2 - 1.0 g) were contacted with excess water (pH 7.5) and allowed to equilibrate under temperature controlled conditions ranging from 8 to 80°C. Swollen gel was measured volumetrically and by weighing after removing excess water phase. Both measurements gave the same results.

The variation of gel volume with temperature is shown for two gels in Fig. 17. At 25°C, polylsoproprylacrylamide is swollen about thirty times

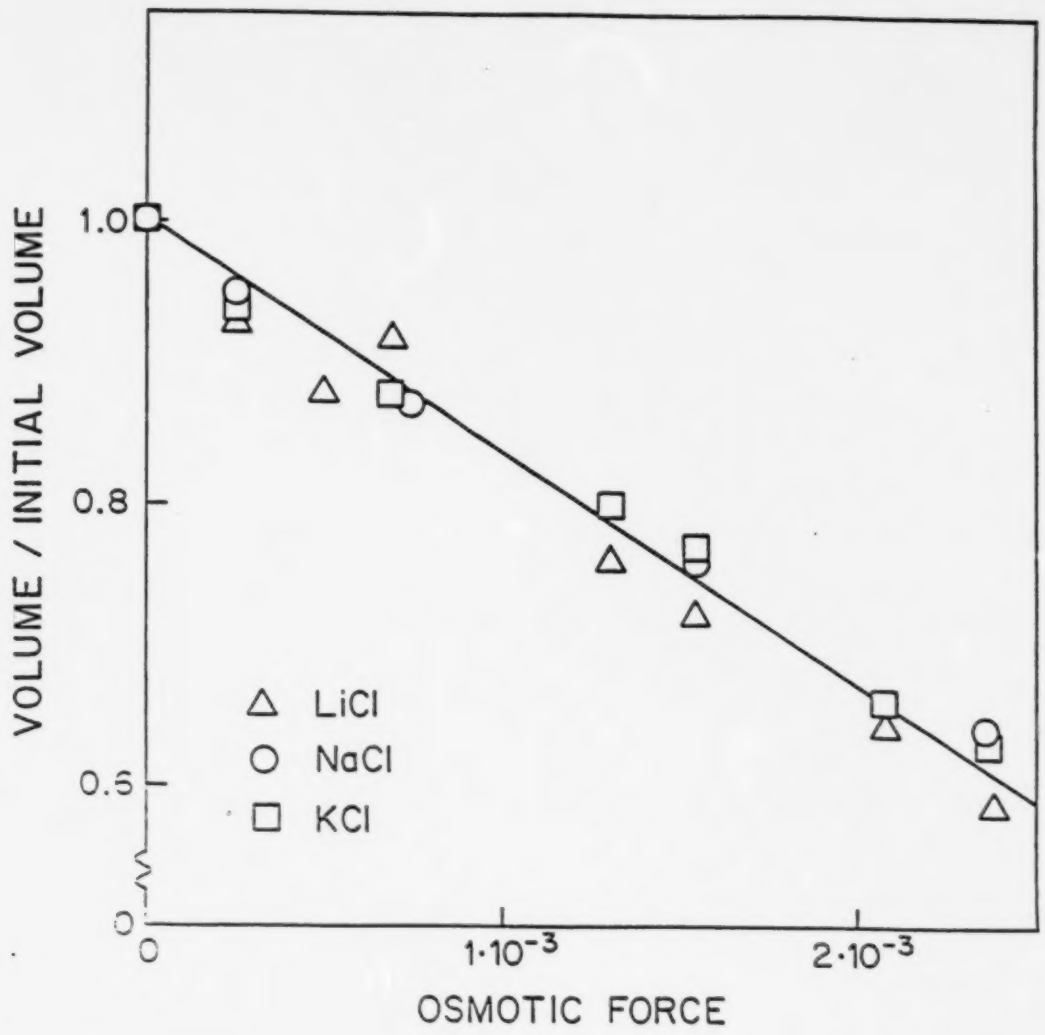


Figure 16 Gel Swelling vs. Added Salt.

its dry weight. The swollen gel shrinks continuously until just above 33°C, when it suddenly collapses to ten percent of its former volume. Above 34°C, the collapsed gel's swelling is a more modest function of temperature. Similarly, at 25°C, the copolymer of diethylacrylamide and sodium methacrylate is swollen to more than fifty times its dry weight. As this gel is warmed, it also shrinks, until at 60°C, its volume is only five percent of that at 30°C. The discontinuity in swelling reported for this type of gel by others (1) was not observed. However, the change in volume per degree of the diethyl gel, which is greatest in the range 50-55°C, is less than the change per degree of the isopropyl gel.

In order to compare the behavior of these gels with that of the hydrolyzed crosslinked polyacrylamide gels, aliquots of polyisopropylacrylamide gels were contacted with acidified and salt solutions. The swelling of polyisopropylacrylamide gel vs. added acid and salt is shown in Table 8. This gel's volume does not change significantly on the addition of modest quantities of acid because the gel is not a polyelectrolyte. Nor does the isopropyl gel's volume vary with added salt at low salt concentration, although it does collapse at high added salt concentration. Typical data for a 5% crosslinked partially hydrolyzed polyacrylamide gel are shown for comparison. Gel volumes decrease dramatically with increasing acid. However, the polyacrylamide gels are not temperature sensitive.

Table 8

Polyisopropylacrylamide Swelling vs. Added Acid and Salt[a]

Added Solution	Relative Volume[b]	Volume of pH[b,c] Sensitive Gel
0 m M Hcl/g gel	1.00	1.00
0.04	1.00	0.33
0.11	0.96	0.15
0.14	0.93	0.11
0.190	0.89	0.07
0.23	0.93	0.05
0.32	0.92	0.04
excess 0.05M NaCl	1.00	1.00
0.10	0.96	0.93
1.00	0.22	0.80
excess 0.05M $CaCl_2$	0.98	

(a) All experiments are at 25°C. the isopropylacrylamide gel was made with 1% crosslinking.
(b) The relative volume is that in solution divided by that in water.
(c) The pH sensitive gel was a partially hydrolyzed polyacrylamide with 5% crosslinking. Similar gels have been reported elsewhere.

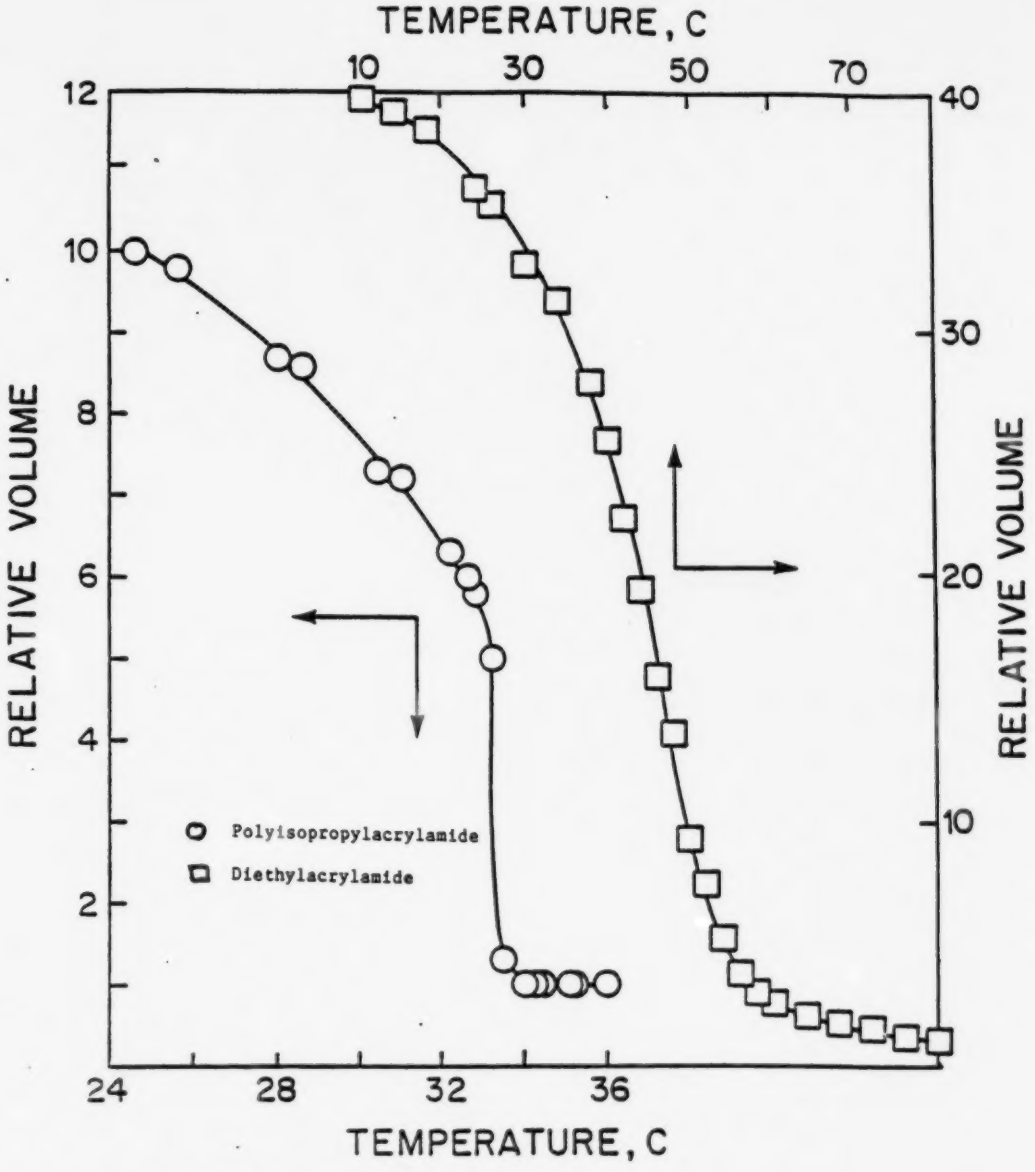


Figure 17. Gel Swelling vs. Temperature

Discussion of Ionic Gels

The ability of partially hydrolyzed crosslinked polyacrylamide gels to swell and collapse in response to externally imposed changes in pH has been demonstrated for a series of gel preparations. The results show that the volume of exchangeable water is affected by both the crosslinker and the acrylamide concentration. These effects are predictable using simplified models that relate swelling capacity to elasticity (crosslink concentration) and concentration of potentially ionizable groups. High density gels, made by using high acrylamide concentration, are physically stronger but do not swell as much.

It has been shown that gel volume to the (-2/3) power is directly proportional to the degree of crosslinking, as suggested by theory. This supports the assertion that gel swelling is a balance between gel elasticity, which is a function of the degree of crosslinking, and the gel ionization, which controls electrostatic forces. However, the model is not completely verified by the data as shown by the fact that the data in Figure 11 and 12 extrapolate to a finite intercept. Such an intercept implies that an uncrosslinked gel would not dissolve, which is incorrect. The apparent intercept may reflect the non-Hookian elasticity characteristic of highly swollen gels, which is a feature of advanced gel theories (12).

Theory shows that gel volume to the (-2/3) power varies with pH as a result of the amount of added acid or base. This prediction is based on the assumption that the charge on the gel comes from ionization of the carboxylic acid, and not from the dissociation of ion pairs. This assumption is consistent with selected titration test results. Titration curves can be used to estimate average pK values of the gel. Typical value of pK is 5.6; this is higher than the pK for acrylic acid but it is close to that of 5.4 for most carboxylic acids. This supports the idea that gel charge comes from acid ionization.

The alternative hypothesis, that gel charge results from ion pair dissociation, has been described (24,25), does not work as well. As a result, ion pair dissociation seems an unlikely explanation of the results.

Discussion of Temperature Sensitive Gel

The dramatic change in gel volume that occurs in response to relatively small changes in temperature of the polyisopropyl and diethyl modified crosslinked acrylamide polymers is reversible. It provides a unique mechanism for extracting a water phase from feed solutions using low level heat. As such it is a promising alternative low energy requirement extraction process.

The results in Fig. 17 show that the modified-polyacrylamide gels contract sharply on warming. The change in volume depends on the substitution groups on the acrylamide group; data presented elsewhere (27) show that volume change also depend on the degree of crosslinking.

The collapse of these gels has been ascribed to changes in solution characteristics with temperature. The gel containing diethylacrylamide is a rough polymeric parallel of triethylamine, which shows critical solution temperature behavior with water in the room temperature range. Lower critical solution temperatures have been reported in uncrosslinked substituted polyacrylamides (32), and are relatively common in polymer

solutions in general. Upper critical solution temperatures have been reported in crosslinked, unsubstituted, partially hydrolyzed polyacrylamide (3).

These observations suggest that the modified polyacrylamide gels are like supercritical solvents. Unlike supercritical solvents, the gels do not require high temperatures and pressures. Like supercritical solvents, the gels' physical properties can change dramatically with small temperature changes.

Detailed thermodynamic calculations of the gel's phase diagram are expected to show isobars with two main regions. In one region, at low temperature, the gel will follow equations roughly parallel to the Flory theory of crosslinked gels (20). For the non-electrolyte isopropyl gel, this theory may include enthalpic and elastic corrections. For the polyelectrolytic co-polymer, this theory will also include ionic corrections. However, the variation of gel swelling with temperature will not be large in this first region. In a second region, at higher temperatures, the usual gel phase boundary will intersect the phase boundary of a lower critical solution temperature. In some cases, this intersection may produce phase transitions like those reported for polyectrolyte gels (1,22,3). We are not certain how to analyze the phase behavior in this second region, but ongoing research is expected to lead to a better understanding and ultimately a more quantitative description of the gel's behavior.

SECTION 7

SELECTIVITY OF GEL EXTRACTION

Theoretical Aspects

The feasibility of using gels to extract water and thereby concentrate aqueous solutions or suspensions rests on the gel's capacity to imbibe water while rejecting solutes and colloids. Gel selectivity is expressed in terms of the efficiency of exclusion; it is defined as the concentration difference C between the initial solution and the raffinate, divided by the maximum concentration difference C_{max} which would be attained if all the solute in the initial solution were recovered in the raffinate. From this definition it follows that:

$$\eta = \Delta C/\Delta C_m = [C_r/C_i - 1] \; / \; [M_i/M_r - 1] \qquad (12)$$

where C_r = raffinate solute concentration
C_i = initial solute concentration
M_r = mass of raffinate
M_i = mass of initial solution

Efficiency is a measure of the degree to which a solute is excluded from the gel as water is absorbed. For example, if half the feed solution is absorbed by the gel phase, and if the raffinate concentration is twice that of the feed, then R is 100%. However, if raffinate concentration remained the same as the feed concentration then R would be 0%, i.e. no separation would have occurred. For practical applications, the degree of swelling is also important. However, the degree of swelling of polyacrylamide gels is so large that applications are likely to be limited by exclusion, not by insufficient swelling. Therefore, η is a useful parameter for characterizing gel performance.

Efficiency of separation incorporates four aspects of separation. First, it reflects the effectiveness of the mechanical separation of the swollen gel from the raffinate; any raffinate entrained between the gel particles represents solute lost to the process. Such losses could be especially significant when raffinate concentrations are high. Entrainment of raffinate can be minimized by proper draining and by applying mild suction pressures or by centrifuging the swollen gel to drain away raffinate. As a last resort, a washing step with pure water could be used. It should be pointed out that incomplete drainage was not a significant problem in the laboratory test work described below.

The other three important elements that can affect separation efficiency have a chemical origin, namely thermodynamic partitioning effects, solute charge effects, and solute size effects.

Thermodynamic partitioning effects are common in liquid-liquid extraction. Such separations are described in terms of a partition coefficient, which is a function of the differences in chemical potential referred to a standard state, often taken as high dilution (33). For example, the chemical potential of bromine dissolved in water is much higher than that in benzene. As a result, when water and benzene are mixed together, the equilibrium bromine concentration in the water phase is much

less than the concentration in the benzene phase. It seems unlikely that this type of thermodynamic partitioning is important in gel extractions. Expanded gels contain more than ten times their dry weight of water. As a result, they consist of at least 90% water. Under these conditions, the chemical potential of a small solute inside the highly swollen gel is not likely to differ much from that in pure water so that this type of partitioning is not likely to have a strong influence on efficiency of separation.

Separations due to solute charge effects are likely to be more significant because the gel is a polyelectrolyte. The gel surface is assumed to be anionic with sodium counterions arranged in the adjacent solution film. To simplify the description, it is assumed that all solutes can be represented as sodium salts of a common monovalent anion. If all mobile ions form ideal solutions, then the constraints of Donnan equilibrium lead to the relation (34,35):

$$[Na^+][A^-] = [Na^+]_o[A^-]_o \tag{13}$$

where $[i]$ and $[i]_o$ are the concentrations of solute "i" inside and outside of the gel, respectively. The sodium ion concentration outside the gel must equal the anion concentration outside because of electroneutrality. The sodium ion concentration inside the gel must balance the anionic charge of $[A^-]$ and the carboxyl ions of the gel itself. Thus

$$([RCOO^-] + [A^+])[A^-] = [A^-]_o^2 \tag{14}$$

where $[RCOO^-]$ is the concentration of gel per volume of swollen gel. The efficiency (η) is defined by:

$$\eta = 1 - \frac{[A^-]}{[A^-]_o} \tag{15}$$

where $[A^-]$ is calculated by solving equation (14)

$$1 - \frac{RCOO^-}{2A_o^-}\left(\left[1 + \frac{4(A_o^-)^2}{(RCOO^-)^2}\right]^{\frac{1}{2}} - 1\right) \tag{16}$$

Note that in this case efficiency is a function of concentration. If the anion is not monovalent but has a charge of (-z), the efficiency can be calculated in a similar way (24,34). All the quantities on the right hand side of Eq. (16) can be measured independently. As a result, the efficiencies expected by Donnan exclusion can be compared with those measured in gel extraction experiments.

The fourth element that can affect efficiency is solute size in relation to the three dimensional structure imposed by the gel's polyacrylamide skeleton. Separations due to solute size are best visualized by imagining that the gel is an expanded mesh. Small molecules can easily penetrate openings in the mesh, but large solutes can not enter. This concept can be expressed quantitatively using excluded volume theory (20). We consider a solute of volume v within a gel volume V. We then imagine inserting crosslinks of zero volume into the gel volume. The probability of

inserting one crosslink without hitting the solute is (1-v/V). The probability of inserting N such crosslinks equals the fraction of the volume accessible to solute (V_s/V):

$$\frac{V_s}{V} = \left(1 - \frac{v}{V}\right)^N \tag{17}$$

$$= \left(1 - \frac{cv}{N}\right)^N \tag{18}$$

where c = N/V is the crosslink density. As N becomes large, this becomes

$$\frac{V_s}{V} = e^{-cv} \tag{19}$$

Next, we imagine that our gel is immersed in an excess of feed solution of unchanged solute concentration $[A]_o$. From a mass balance on A it follows that

$$\frac{A}{A_o} = \frac{V_s}{V} \tag{20}$$

substitution into equation (15) leads to the prediction that:

$$\eta = 1 - e^{-cv} \tag{21}$$

where [A] is the actual solute concentration in the gel. If we assume that c is proportional to the amount of crosslinking agent, then we can correlate the separation efficiency with the amount of crosslinking. V represents the volume available for solute and is expected to be related to the acrylamide concentration.

Effect of Gel Composition

Gel selectivity as a function of crosslink fraction and acrylamide concentration was investigated. The solutes used in these experiments were Vitamin B12 (molecular weight 1355) and two separate polyethylene glycols having molecular weights of 400 (PEG 400) and 3,400 (PEG 3400) deltons (Table 4). Vitamin B12 (Sigma Chemical Company) had a purity of 99%; further purification did not effect the results. PEG's were obtained from Aldrich Chemical Co.; molecular weights vary within 10% of the nominal value.

Aliquots (0.1-0.5 dry gel) of each of the formulations listed in Table 5 were contacted with appropriate solutions and allowed to equilibriate for 1.5 hours on a shaker to ensure good contracting. The gel phase was separated from the raffinate by decanting and measured. The procedure is illustrated in Figure 18.

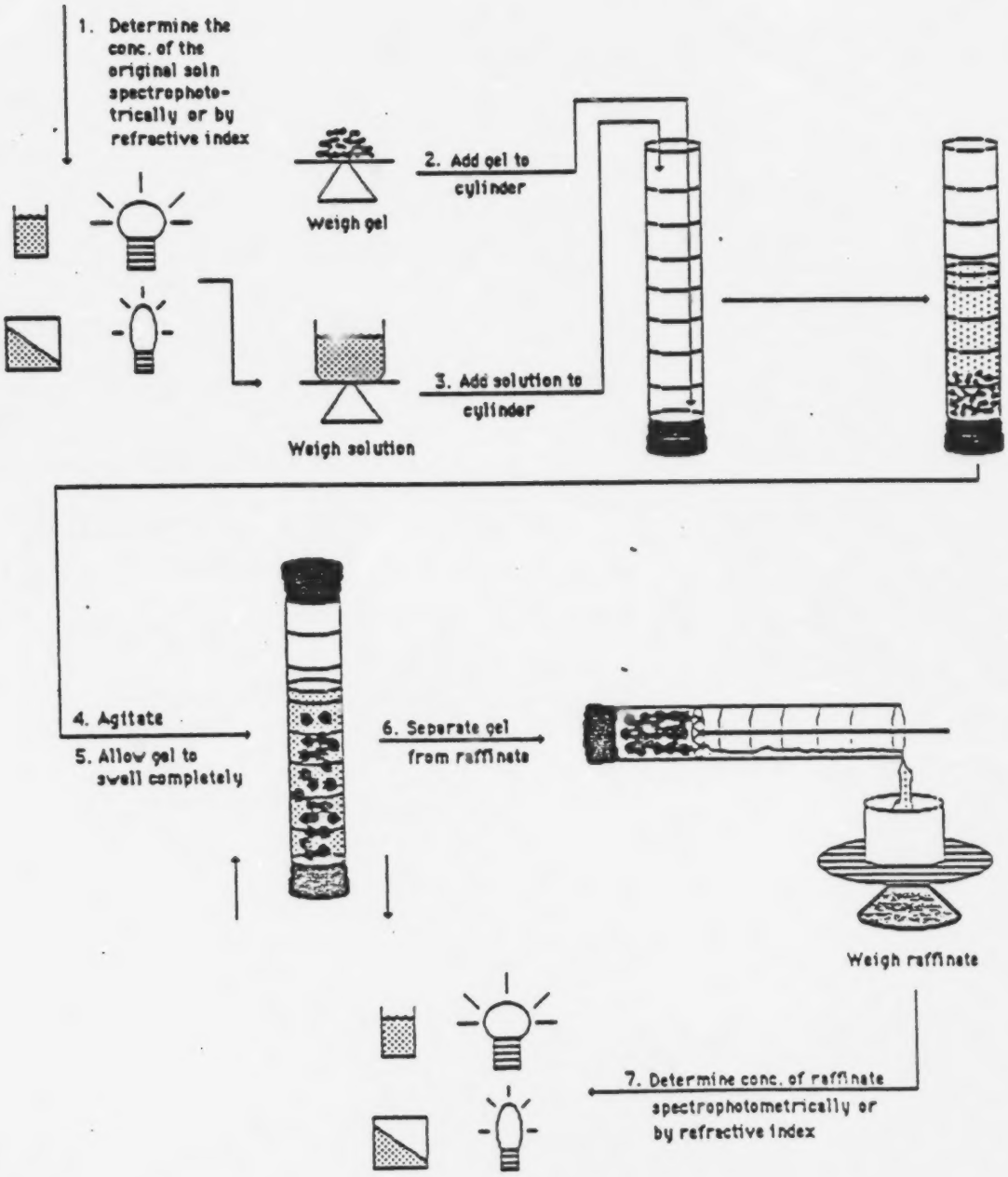

1. Determine the conc. of the original soln spectrophotometrically or by refractive index
Weigh gel
2. Add gel to cylinder
Weigh solution
3. Add solution to cylinder
4. Agitate
5. Allow gel to swell completely
6. Separate gel from raffinate
Weigh raffinate
7. Determine conc. of raffinate spectrophotometrically or by refractive index

Figure 18 Extraction procedure for the determination of η.

It was noted that physical separation of raffinate from the gel phase was more difficult with smaller size gel particles and resulted in increased entrainment of raffinate with the gel phase. Use of larger gel particles minimized this problem but resulted in somewhat longer equilibration times. The time for equilibration was estimated from

$$\frac{l^2}{D\ t_e} \ll 1$$

where l is the characteristic particle dimension or equivalent diameter, D is the diffusion coefficient, and t_e the swelling time to reach equilibrium.

Results for the three solutions are summarized in Figures 19, 20 and 21 using the relationship defined by equation (21); values of $-\ln(1-\eta)$, calculated from measured changes in concentration, are plotted as a function of the product of crosslink fraction (c) and acrylamide concentration (v). The insets in each figure show the percent efficiency plotted against crosslink fractions.

It is clear that higher rejection efficiencies can be obtained using more highly crosslinked polymers. Vitamin B12 solutions show very low rejection efficiencies with low crosslinked polymers. Higher rejection efficiencies were observed with more highly crosslinked gel preparations. PEG 3400, which is a larger molecule showed higher rejection efficiencies in all cases. PEG 400 gave intermediate results.

Figures 19 and 20 show that $-\ln(1-\eta)$ is essentially linearly related to polymer composition as predicted by equation (21). The PEG 3400 test results show considerable scatter at low crosslink concentration but follow the same trend. These findings indicate that:

(a) Gel's selectivity can be altered to suit conditions by adjusting the amount of crosslinker and solvent (water) used in making gels. Changing solvent concentration is equivalent to changing acrylamide concentration and hence changing the gel's packing density which in turn affects the gel's potential for expansion. Thus both acrylamide concentration and crosslinkage concentration affect the potential for volume expansion.

(b) Comparison of the PEG 400 and PEG 3400 solutes shows that the larger molecular weight (size) solute gives higher rejection efficiencies. This is consistent with the concept that the gel's skeletal openings restrict entry of larger molecules but allow free passage of small molecules. Molecular shape is also a factor. Vitamin B12 is a compact molecule whereas PEG molecules are extended. This may account for the lower efficiency of Vitamin B12.

(c) Higher efficiencies of gels that have higher concentrations of crosslinking agent and/or acrylamide in the original mixture have been ascribed to the gel structural properties, namely smaller skeletal openings due to more crosslinking and smaller volumetric expansion potential.

Effect of Solute Size

This phase of the research program was designed to study the use of crosslinked gels as size selective extraction solvents. Two commercially available gels were used. Biogel P-6 is a partially hydrolyzed crosslinked polyacrylamide gel; it has a particle size in water of $150\text{-}300\times10^{-6}$ m; it is used for gel permeation chromatography (Bio-Rad Laboratories). It was

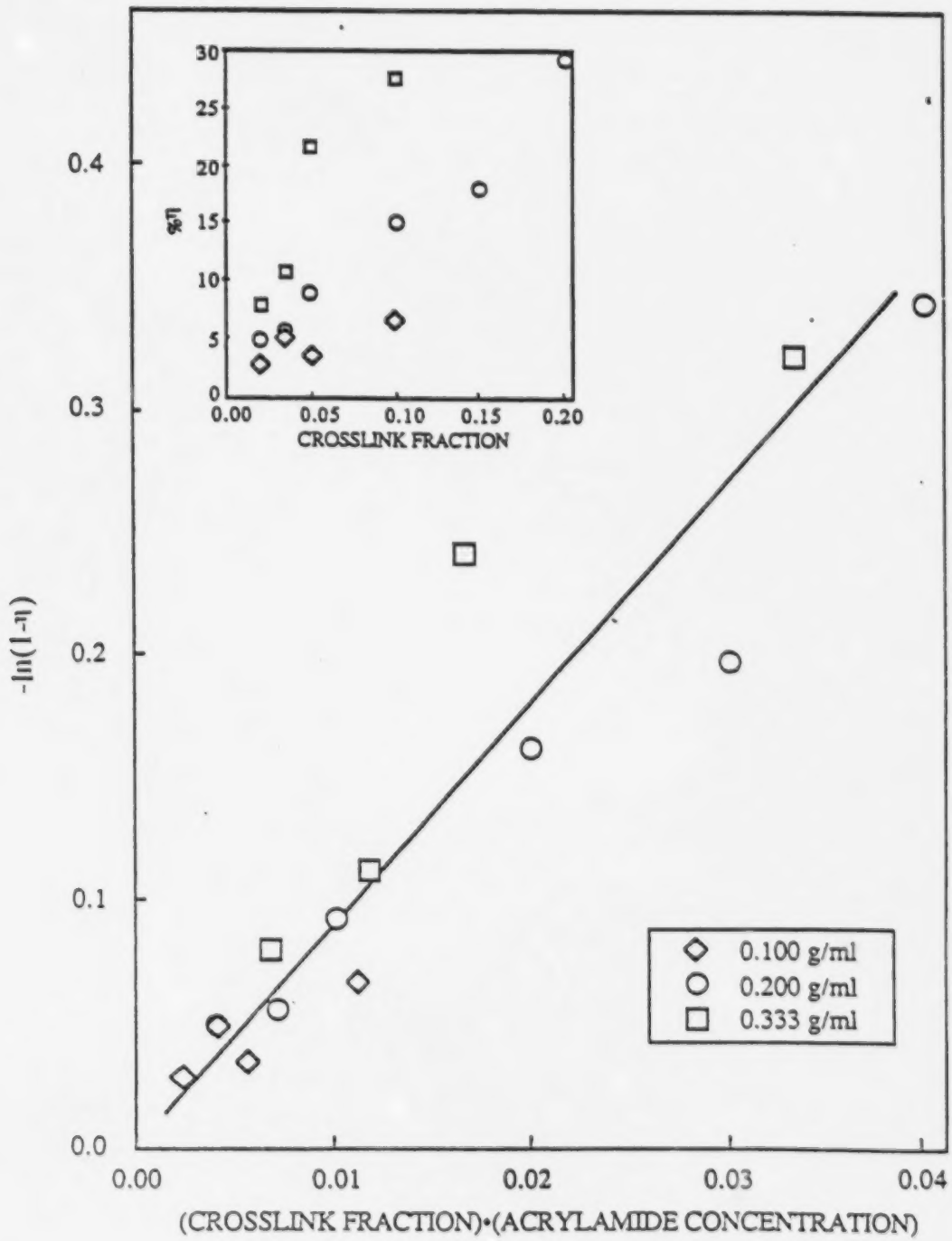


Figure 19 Results for vitamin B_{12} extractions showing η as a function of crosslink fraction acrylamide concentration.

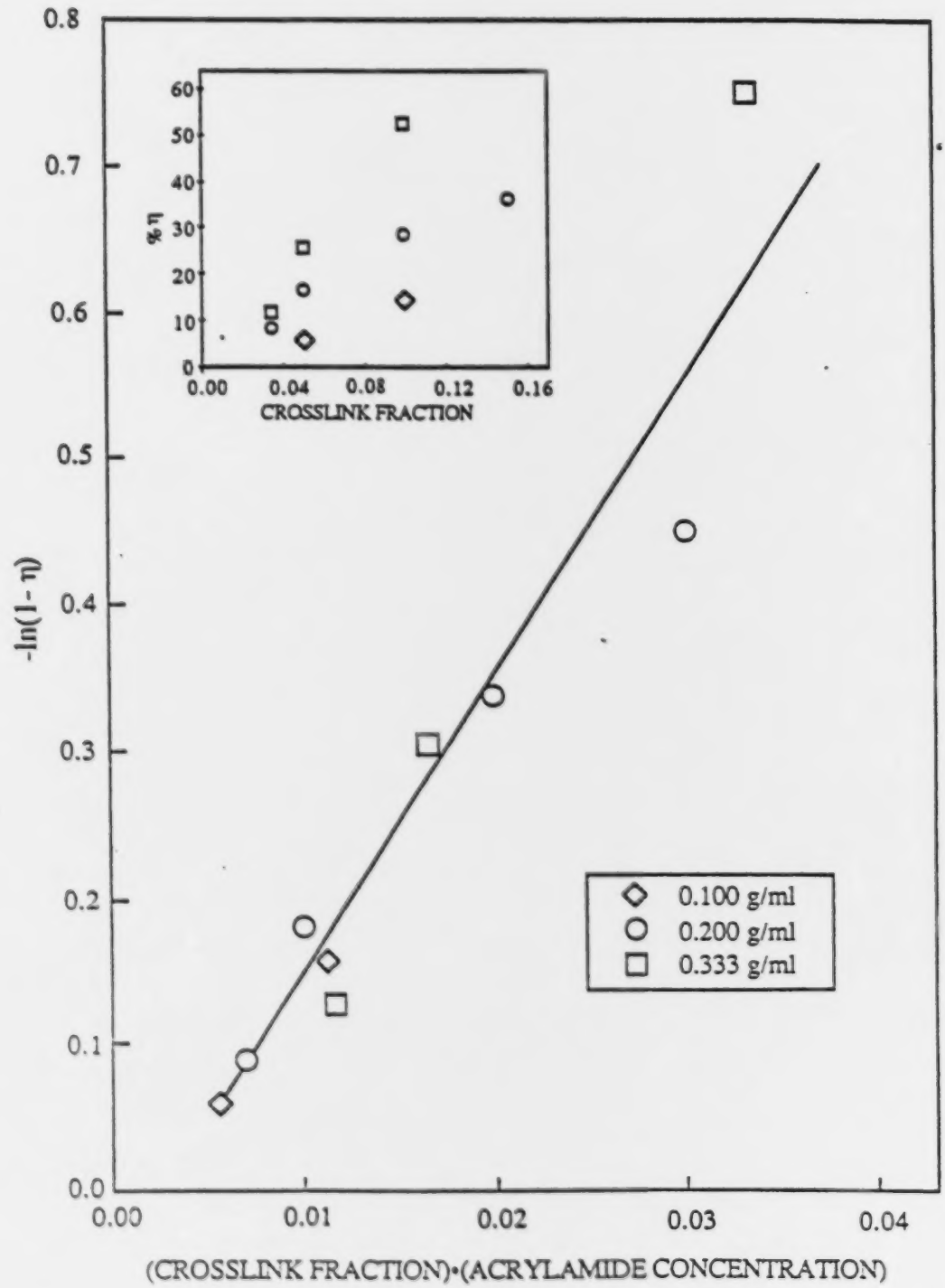


Figure 20 Results for PEG 400 extractions showing η as a function of crosslink fraction acrylamide concentration.

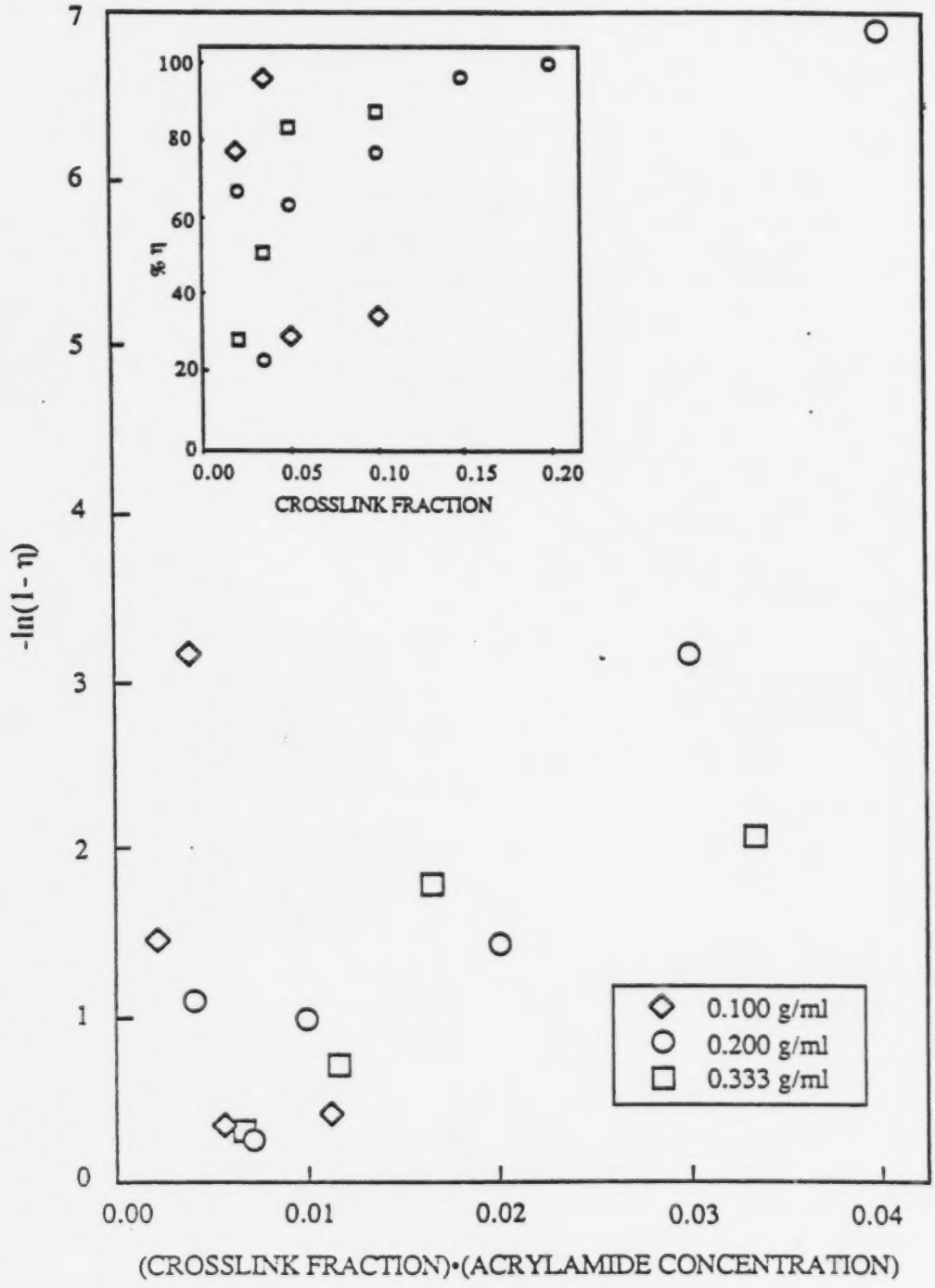


Figure 21 Results for PEG 3400 extractions showing η as a function of crosslink fraction acrylamide concentration.

hydrolyzed in our laboratory for 24 hours at 323°K in 0.5 M Na_2CO_3. The second gel (CM Sephadex C-50) was purchased from Pharmacia Fine Chemicals). This material is also made for gel permeation chromatography and has a dry particle size of $60\text{-}120 \times 10^{-6}$ m. It was not hydrolyzed because it comes as a weakly ionic material.

A selection of different molecular weight solutes were tested as shown in Table 9. The source and pretreatment of solutes has been described elsewhere (3). The results in Table 9 show that solutes which are larger than 3 nm in diameter were rejected with an efficiency of at least 80%. These experiments were carried out with feed concentrations in the .08 to 3 molar range. As a result, entrainment of even small quantities of raffinate has significant effects. For example, when the 34.6 nm latex solution was tested, the efficiency of rejection was increased from 82% to 97% by mildly washing the expanded gel displace raffinate and to remove latex particles that adhered to the gel.

The effect of molecular size and shape on rejection efficiency is illustrated in Figure 22. Results on five different molecular weight size fractions of polyethylene glycol are shown on a semilogarithmic plot. The efficiencies observed are found empirically to be proportional to the logarithm of the glycol's molecular weights. While there is no convincing theory for this semi-logarithmic behavior, it is recognized that similar effects occur commonly in gel permeation chromatography. The lower efficiencies of sucrose and urea separation have been ascribed to shape effects as discussed in a previous section comparing the behavior of Vitamin B12 and PEG.

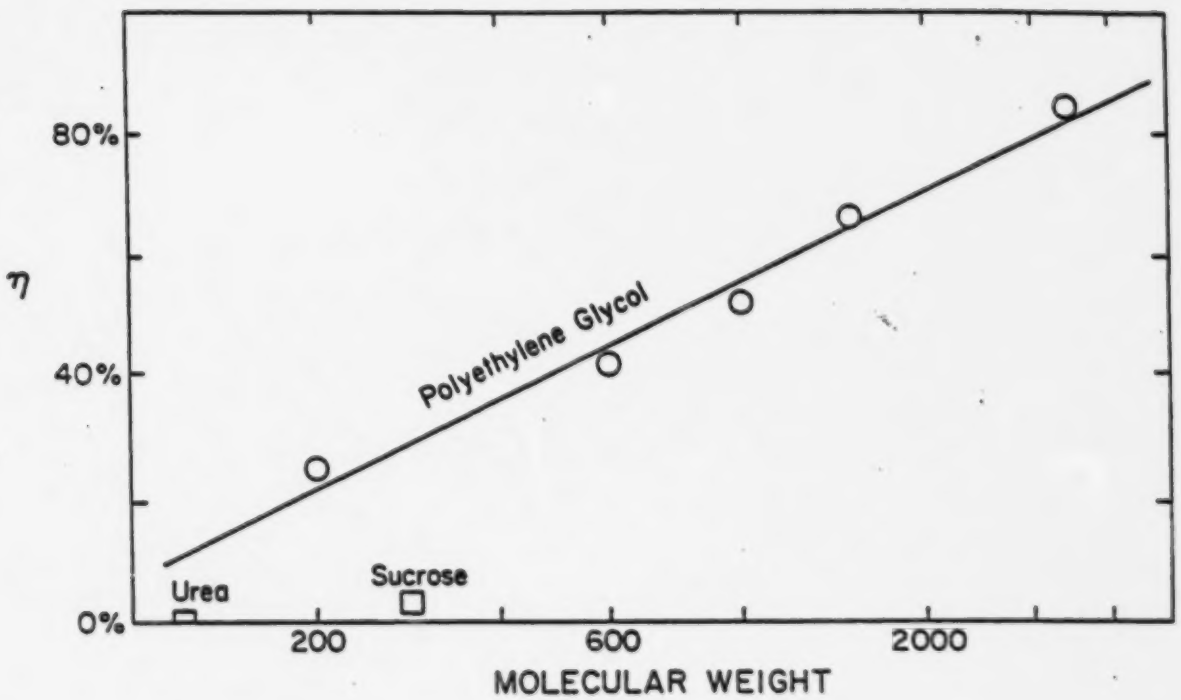


Figure 22 Separation Efficiency Depends on Solute Shape.

Table 9

Concentration of Aqueous Solutions Using Hydrolyzed Polyacrylamide Gels

Solute	Mol. Wt. Daltons	Solute Size, nm	Feed Conc., Wt.%	Raffinate Conc., Wt.%	Percent Efficiency
Polystyrene Latex	--	990[a]	0.21	0.35	85
Polystyrene Latex	--	34.6[a]	0.91	1.40	82
Silica	--	5[a]	1.82	3.03	80
Bovine Serum Albumin	66,000	7.2[b]	.08	.18	93
Hemoglobin	64,500	6.2[b]	0.73	1.26	91
Polyethylene Glycol	3,000-3,700	3.8[c]	0.56	1.09	6
Sucrose	342	.84[b]	1.00	1.09	6
Urea	60	.53[b]	3.00	3.00	0

(a) Measured by electron microscopy.
(b) Estimated from the diffusion coefficient in water using the Stokes-Einstein equation.
(c) Reported by the manufacturer from light scattering measurements.
(d) Dextran gel (Sephadex C-50).

It should be pointed out that all the solutes in Table 9 are neutral or negatively charged at the pH of separation. When cationic proteins such as lysozyme and cytochrome C were tested, they precipitated on the gel and were therefore not concentrated in the raffinate. The gel's swelling capacity was not affected. The dextran gel gave similar results as the polyacrylamide gel.

Effects of Solute Charge

This part of the experimental program focused on the study of ionized solutes with different negative charge densities. The solutes are listed in Table 10 along with their molecular weights and potential charges. Most of the experiments were made on aliquots of the P-6 gel described in the previous section.

The results in Table 10 show that solutes are best separated if they are highly dilute, multiply charged, and without added salt. For example, 10^{-4} M divalent congo red is more efficiently separated than 10^{-4} M monovalent bromocresol green. The efficiency of separating methyl orange is 97% at 10^{-4} M, but only 55% in the presence of 0.1 M NaCl. The separations depend much more on the total salt present than on the chemistry of individual ions; the efficiency of separating methyl orange or sodium chloride is equally good at 10^{-4} M total salts, but equally poor at 0.1 M total salts.

These observations are consistent with predictions based on Donnan equilibria as summarized by Eq. (16). This equation predicts that separation efficiency is highest for highly dilute solutes present without added salt. The equation implies that the efficiency is not affected by the chemistry of the small ions, but by the concentration of charged groups within the gel, $[RCOO^-]$.

Eq. (16) was used to predict efficiencies from measured concentrations of $[RCOO^-]$ in the gel. $RCOO^-$ was measured by titration to be 3.5 meq/g dry gel. Predicted values of η based on Donnan equilibrium are shown in Table 10 next to values of η calculated from experimental measurements. For dilute monovalent solutes, predicted values lie close to, but slightly above, experimental efficiencies. For example, for 10^{-4} M NaCl, the predicted efficiency is above 99%, whereas the experimental value is 97%. One possible explanation is that efficiencies measured experimentally are slightly compromised by liquid entrained between the gel particles, i.e., incomplete separation of raffinate.

Comparison of predicted and measured efficiencies for monovalent solutes are in agreement. For polyvalent solutes, theoretical efficiencies are often much higher than experimentally measured ones. This probably reflects incomplete ionization of solutes at the pH of the experiment. For example, if we assume that trypan blue has only two of its four potential charges ionized, the theoretical and experimental efficiencies are in much closer agreement. Unfortunately, pH values were not measured in these tests.

Temperature Sensitive Gels

This part of the program looked at the selectivity of the modified nonionic polyacrylamide gels that were described in the previous section on volume changes of Temperature Sensitive Gels. Procedures were essentially the same as described previously except that concentration of solutes were measured along with changes in volume. The swollen gel was separated from the raffinate by filtration through a steel screen, and both gel and raffinate were weighed. The gel was then collapsed by warming, and the extract was separated. The concentrations of both raffinate and extract were analyzed. Table 11 lists the solutes tested; most of the solutes are neutral species ranging from small molecules to a molecular weight of 2×10^6 for Blue Dextran. Three gel preparations were tested. Efficiencies for gel extractions are summarized in Table 11. The efficiencies were measured in triplicate and are accurate within ± 3%. The three gels have different degrees of crosslinking as shown. While all extractions were run at 25°C the polyisopropylacrylamide was regenerated at 35°C, and the two gel copolymers of diethylacrylamide and sodium methacrylate were regenerated at 60°C.

TABLE 10

SEPARATION OF CHARGED SOLUTES WITH PARTIALLY HYDROLYZED POLYACRYLAMIDE GELS[a]

Experiments used the hydrolyzed P-6 gel except as indicated.

Monovalent Test Solutes	Additional NaCl	η (expt)	η (Donnan)[b]	Polyvalent Test Solutes	Additional NaCl	η (expt)	η (Donnan)[b]
10^{-4} M NaCl	-	97%	> 99%		-		
10^{-4} M Methyl Orange	-	97%	> 99%	10^{-4} M Congo Red	-	97%	> 99%
10^{-4} M Bromocresol Green	-	94%	> 99%	10^{-4} M Trypan Blue	0.05 M	96%	> 99%
				10^{-4} Trypan Blue	0.1 M	83%	> 99%
				10^{-4} Trypan Blue	0.1 M	73%	97%
$2 \cdot 10^{-4}$ M Sodium salt of pentachlorophenol (c)	$3 \cdot 10^{-3}$ M	65%	69%	10^{-4} Congo Red	0.1 M	71%	79%
10^{-4} M Methyl Orange	0.1 M	55%	49%	10^{-4} M Trypan Blue	0.2 M	69%	92%
0.1 M NaCl	-	55%	50%	10^{-4} Trypan Blue	0.3 M	52%	89%
10^{-4} M Methyl Orange	0.9 M	14%	18%	10^{-4} Congo Red	0.9 M	34%	36%

(a) Molecular weights and potential charges of the less familiar test solutes are as follows: methyl orange (327,-1); bromocresol green (720,-1); pentachlorophenol anion (265,-1); congo red (697,-2); trypan blue (961,-4).

(b) These values are calculated from Eq. (3) assuming that the test solutes are completely ionized.

(c) This experiment used a partially hydrolyzed polyacrylamide polymer synthesized with 5% crosslinks. The added electrolyte here is NaOH.

The results in Table 11 show that the gels do not reject low molecular weight solutes like urea but exclude the high molecular weight solutes like ovalbumin. Small solute molecules like urea, pentachlorophenol, and Vitamin B12 can move into the gel between the strands of the skeletal mesh, just as if the mesh were a large size sieve. Larger solutes like ovalbumin, polystyrene latex, and large molecular weight PEG are excluded, just as larger particles would be rejected by a sieve with size openings smaller than the particle.

Table 11

Selectivity of Extractions Using Temperature Sensitive Gels

Solute	Mol. Wt.	Polyisopropyl-acrylamide	Copolymer of Diethylacrylamide and Sodium Methacrylate	Copolymer of Diethylacrylamide and Sodium Methacrylate
		1 (a)	4 (a)	2 (a)
Urea		2	3	2
Sodium Pentachloro-phenolate	267	18	51	--
Vitamin B12	1,355	32	15	7
Ovalbumin	45,000	97	84	
Polyethylene Oxide	600,000	96	89	92
Gelatin		98	97	
Blue Dextran	2,000,000	97	99	96
Polystyrene Latex		95 (b)	96 (b)	96 (c)
Polyethylene Glycol	400	10	5	
	3,400	30	19	11
	8,000	56	25	16
	18,500	80	61	48

(a) Percent of crosslinkage used in preparation.
(b) This latex had a diameter of 0.06 μm.
(c) This latex had a diameter of 1.2 μm.

The gels' separation capacity for different molecular weight (size) solutes is illustrated by the progressively higher efficiencies for the series of polyethylene glycols shown at the bottom of Table 11. The PEG fractions are similar chemically, and differ principally in their molecular weight and hence size. Efficiency values in the 10% range are insignificant and indicate that these molecules can penetrate into the gel freely. In contrast, PEG with a molecular weight of 18,500 is rejected as evidenced by an 80% efficiency under the same conditions. If the mechanical sieve analogy of gel exclusion behavior

is correct, then gel efficiency should increase as the percent of crosslinking is increased. This hypothesis was tested by preparing polyisopropylacrylamide gels with different concentrations of crosslinkage. These gels were tested with solutions of Vitamin B12 and PEG-3400. The results expressed in terms of efficiency are summarized in Figure 23.

The efficiency for separating vitamin B12 doubles as the percentage crosslinking increases from one to six percent. A similar trend is shown for PEG-3400. Noting that molecularly compact vitamin B12 and the extended polyethylene glycol molecule have the same increases in efficiency suggests that the effect is not a strong function of molecular shape. Nevertheless, molecular shape and/or composition appears to have some effect as evidenced by the fact that exclusion efficiencies for vitamin B12 are essentially the same as those of the two fold larger molecular weight PEG 3400 fraction.

Comparison of exclusion efficiencies obtained with temperature sensitive and ionic gels shows that increasing crosslink concentration increases rejection efficiency in all cases. However, the data in Figure 21 indicate that the ionic gels give consistently higher rejection efficiencies of PEG 3400 solutes than the polyisopropylacrylamide gels at the same crosslink concentration (Figure 23). On the other hand, Vitamin B12 test results in Figure 23 show consistently higher rejection efficiencies than the ionic gels in Figure 19. This reversal indicates that other forces related to chemical composition and molecular structures are also important even though size exclusion and ionic effects are predominant.

In order to assess the application of gel extraction over a broader range, a series of progressively higher feed solutions were tested. Gelatin solutions ranging to 8 wt% were tested using polyisopropylacrylamide gels. As shown in Figure 24, highest efficiencies were obtained with the lower feed concentrations. For example, the efficiency obtained with 0.5 wt. % feed solutions is above 95%. At these concentrations, gels offer an excellent method for removing water. However, as the gelatin concentration increases, separations are less successful; for a feed containing 5 wt. % gelatin, the separation is only 60% efficient.

Discussion

Process evaluation of gels made with different concentrations of crosslinkage and acrylamide concentrations show that both the gels' expansion capacity as well as its selectivity are affected. The results are consistent with theory and lead to the interpretation that solute molecular size and gel skeletal openings are the dominant factors that regulate rejection of uncharged solutes such as PEG and Vitamin B12. It follows that gel preparations can be tailored to specific needs.

There is a tradeoff between gel expansion capacity which determines the amount of water that can be extracted per unit weight of gel and the selectivity or rejection efficiency. Since most gels expand by a factor of 10 or more, it would appear that optimization of selectivity is likely to be the more critical factor in process application.

The observations that negatively charged (ionized) solutes are excluded much more effectively than neutral species is a clear indication of a second mechanism of rejection. As indicated in the discussion of gel expansion, ionization of carboxyl groups, -COOH --> $-COO^-$ appears to be the major driving force that leads to imbibing water and attendant expansion of the gel phase. The electrostatic forces involved in expansion are also believed to be

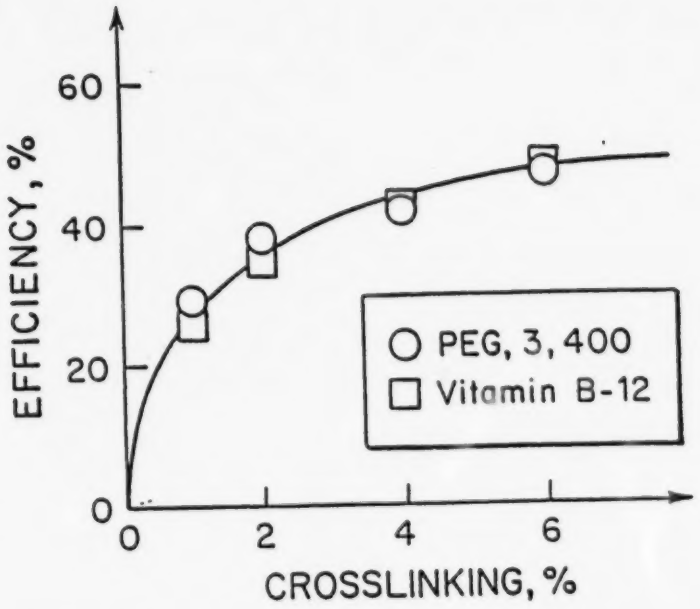


Figure 23 Effect of Crosslink Concentration on Efficiency

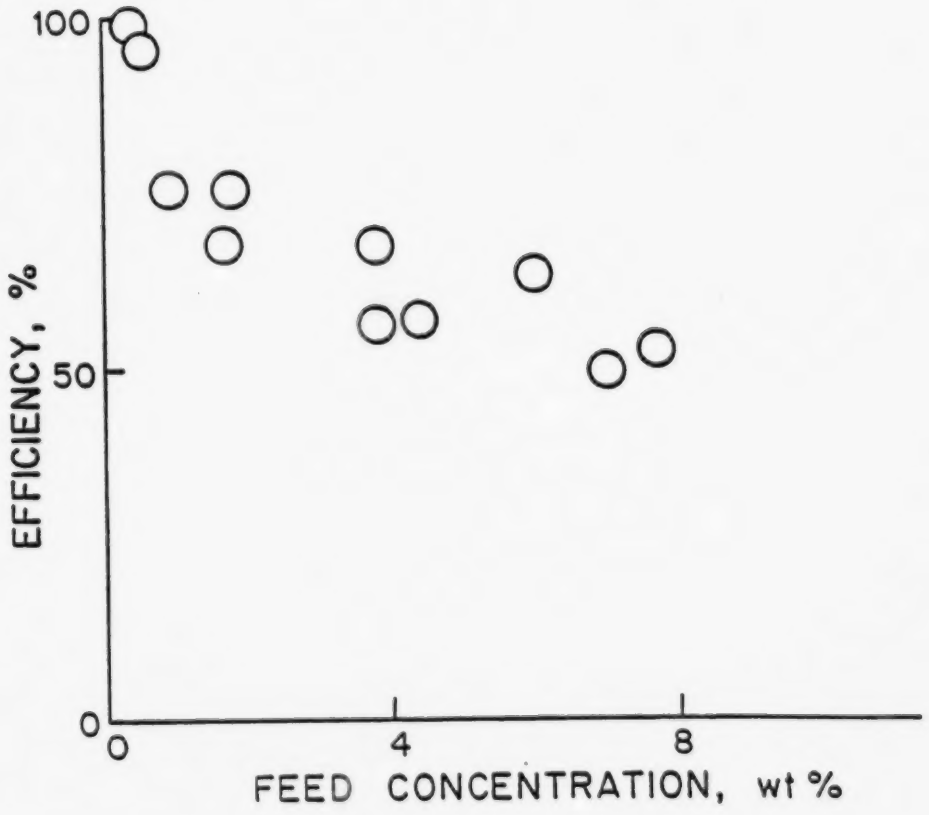


Figure 24 Gel Concentrating Efficiency Using Polyisopropylacrylamide

responsible for the rejection of negatively charged solutes. The concept of charge repulsion as a second mechanism for exclusion of molecules is reasonable and finds analogues in separation phenomena observed in membrane separation processes (36).

The analysis based on Donnan equilibrium appears to describe electrostatic exclusion effects quantitatively. Extension of the theory to account for the effects of added salt solutions is also in accord with experimental results. The loss of efficiency with increasing salt concentration is significant and imposes limits on practical applications of the gel extraction process. Separations that rely on solute rejection associated with electrostatic effects as opposed to size exclusion effects, will be compromised at high salt concentrations. However, as shown in Table 8, salt addition had very little effect on swelling properties of the temperature sensitive nonionic gels. Corresponding studies to measure the effects of salt concentration on rejection efficiencies have not been made. It appears likely, that salt effects will have little or no effect on solute exclusion associated with size effects. At very large ionic strengths, compression of the water boundary layer surrounding particles and or the skeletal surfaces of the gel may become important and result in less efficient rejection of uncharged species.

SECTION 8

PROCESS STUDIES

Solutions of Trace Metals

Removal of trace metal pollutants from industrial and municipal aqueous waste streams is a major problem. Efficient and low cost technological solutions are needed to purify wastewaters prior to discharge to the environment and facilitate recovery of metals. Use of gels for treating aqueous solutions of metals was therefore investigated.

The study of solutions of metals differs from that of organics in that chemical composition of the prevailing species changes very dramatically with pH; metal-hydroxo complexes are formed and solubility is limited; metal-organic complexes are frequently encountered, they usually result in increased solubility. The different species exhibit a range of ionic charges ranging from +2 and +3 for the pure metal ions to negative charges for ionic and hydroxo complexes. This variability in ionic charge density and sign is a critical factor in gel extraction because rejection efficiency is affected by ionic charge. The first step in the study of metal extraction therefore focused on describing the chemistry and solubility of a model compound. Zinc was chosen as a model element because it is a divalent metal, it is only slightly soluble, it forms metal chelates with inorganic chelating agents, and it is strongly complexed by organic complexing agents.

Zinc Solution Chemistry

Zinc ions (Zn^{+2}) are only slightly soluble except at low pH conditions. The solubility product of zinc hydroxida (pKsp) is 17.2 (37)

$$Zn(OH)_2 \dashrightarrow Zn^{+2} + 2OH^-$$

As shown in Table 12, this means that there are essentially no free zinc ions (Zn^{+2}) at pH > 8. Zinc is known to form hydroxy complexes in aqueous environments as shown in Table 13 (37,38). Low pH conditions favor Zn^{+2} as shown by the ratios in columns A, B and C,

Table 12

Solubility of Zinc in the Presence of Hydroxyl Ions

pH	OH^-	Zn concentration m/ℓ	Zn concentration mg/l
2	10^{-12}	6.3×10^{6}	4.1×10^{11}
4	10^{-10}	6.3×10^{2}	4.1×10^{7}
6	10^{-8}	6.3×10^{-2}	4.1×10^{3}
8	10^{-6}	6.3×10^{-6}	4.1×10^{-1}
10	10^{-4}	6.3×10^{-10}	4.1×10^{-5}
12	10^{-2}	6.3×10^{-14}	4.1×10^{-9}

Table 13

Zinc Hydroxy Complexes (38,39)

Reaction	log k (25°C)
A) $Zn^{+2} + OH^- \rightarrow Zn(OH)^+$	5
B) $Zn^{+2} + 2OH^- \rightarrow Zn(OH)_2^\circ$	8.3
C) $Zn^{+2} + 3OH^- \rightarrow Zn_2(OH)^{+3}$	13.7
D) $2Zn^{+2} + OH^- \rightarrow Zn_2(OH)^{+3}$	5.5

Distribution of Zinc Species Calculated from K Values Listed Above

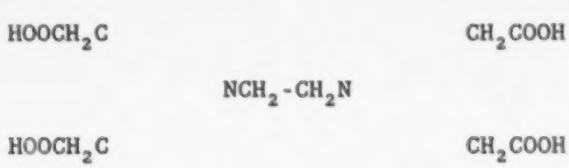
pH	OH^-	(A) $\frac{Zn^{+2}}{Zn(OH)^{+1}}$	(B) $\frac{Zn^{+2}}{Zn(OH)_2^\circ}$	(C) $\frac{Zn^{+2}}{Zn(OH)_3^-}$
6	10^{-8}	1000	$5x10^{7}$	$2x10^{9}$
7	10^{-7}	100	$5x10^{5}$	$2x10^{7}$
8	10^{-6}	10	$5x10^{3}$	$2x10^{4}$
9	10^{-5}	1	$5x10^{+1}$	$2x10^{+1}$
10	10^{-4}	.1	$5x10^{-1}$	$2x10^{-2}$
11	10^{-3}	.01	$5x10^{-3}$	$2x10^{-5}$

which are calculated from the corresponding values of K. Basic conditions favor hydroxy species; at pH 9 monovalent $Zn(OH)^{+1}$ and divalent Zn^{++} are at equal concentration; hydroxy species with charges of +1, 0, and -1 become predominant at higher pH. These changes in ionic charge with pH may be important because they affect rejection efficiency of small solutes by the ionized gels in basic solutions. An equally important aspect of hydroxy formation is that they compete with EDTA as ligands for complexing zinc at pH > 9.

EDTA Solution Chemistry

Ethylene diamine tetraacetic acid (EDTA) was used as a model organic ligand because its chemistry is well defined, it is a strong complexing agent, and it is widely used for complexing metal ions (39). EDTA is moderately soluble, 0.2

g/l at 22°C; its solubility increases at higher pH (40). EDTA ionizes by releasing up to four H^+ ions, one from each carboxyl group.



Ionic charge is therefore pH dependent. The pH distribution of charged species is shown in Figure 25. $EDTA^{-4}$ predominates above pH 10. At pH 8, $EDTA^{-3}$ predominates. At neutral pH there is a small amount of $EDTA^{-2}$. With reference to gel extraction, this means that free EDTA is negatively charged at all pH levels of interest and is therefore susceptible to separation by ionic polyacrylamide gels.

EDTA-Zn Complexes

The chemical model of complexation shows the association of one atom of zinc per molecule of EDTA (40); $EDTA^{-4} + Zn^{++} \rightarrow [EDTA\text{-}Zn]^{-2}$. The high value of the reported absolute stability constant ($\log K = 16.44$) indicates essentially complete complexation of Zn^{+2} provided there is a slight excess of EDTA. Although the residual charge of the complex is pH dependent as shown below:

$$[EDTA\text{-}Zn]^{-2} + H^+ \rightarrow [EDTA\text{-}Zn]^{-1} \qquad \log K = 3.0$$

the K value of 3.0 indicates that the residual charge on the complex is always -2 in the pH range of greatest interest (pH 5-10). Accordingly, the complex should be susceptible to separation by extraction with ionic gels.

Gel Extraction of EDTA-Zn Solutions

Zinc solution ranging from 1000 to 25 mg/l were prepared by dissolving reagent grade zinc in HCl. EDTA was added to give a 10% molar excess over zinc, there being no other significant metal ions present. Solution pH was adjusted using 0.1 N NaOH. Aliquots (0.08 g) of unwashed dry PAC-1 gel were added to each solution (20 ml) and allowed to equilibriate. Raffinate was removed by sieving which retained the expanded gel phase. pH and zinc were measured. Zinc was measured by atomic absorption as discussed in the section on Analytical Procedures. The results are summarized in Tables 14 and 15.

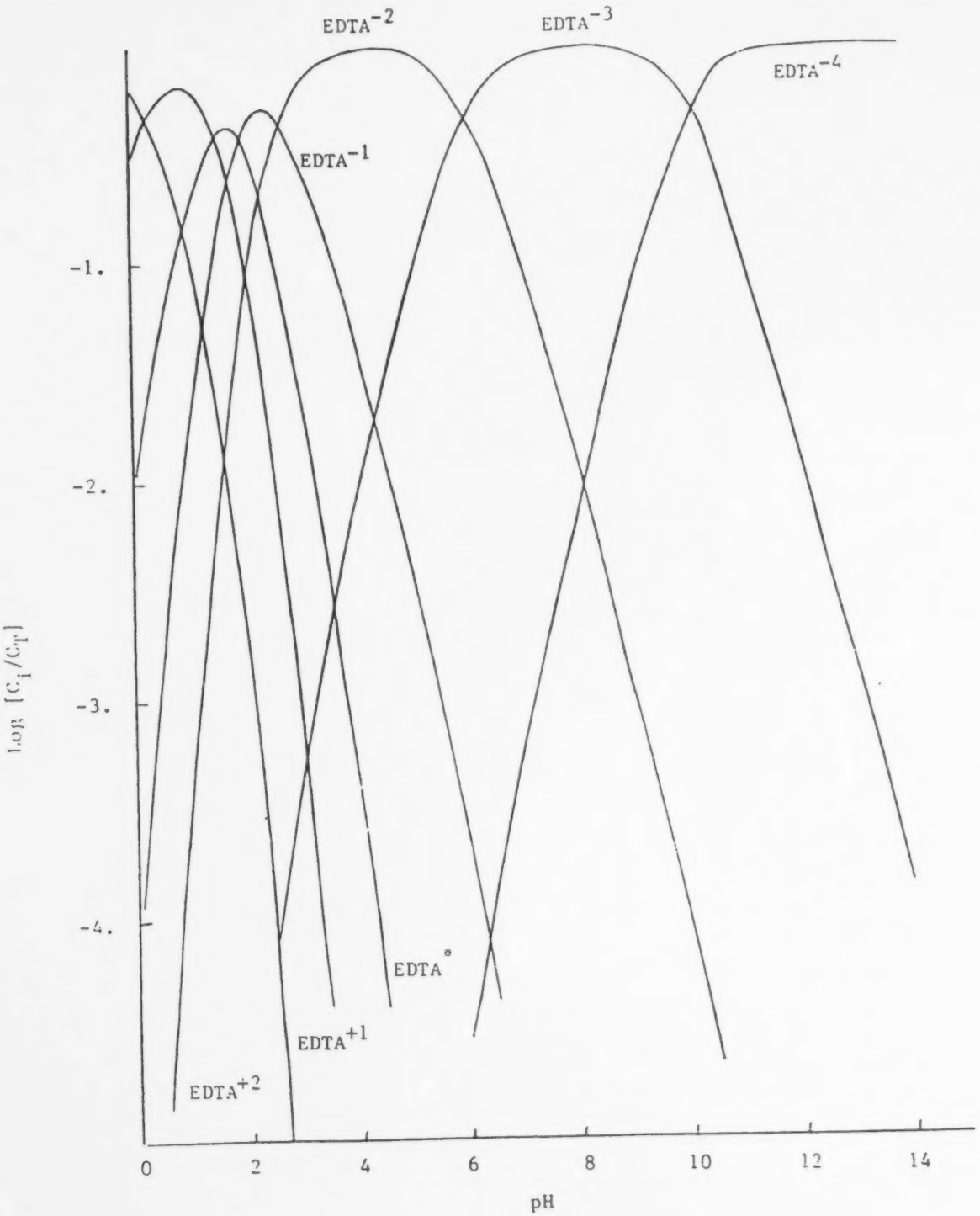


Figure 25 EDTA Ionization Versus pH

Table 14 Zinc Rejection Using pH Sensitive Gels

Zn Concentrations		pH		Gel Phase	
Feed mg/l	Raffinate mg/l	Feed	Raffinate	Expansion Ratio	Rejection Efficiency %
821	858	8.1	6.1	32	30
493	514	8.0	7.7	35	24
76	85	8.0	8.6	55	36
71	80	7.9	8.7	52	45
45	52	8.0	8.5	63	40
19	28	7.9	9.1	72	71

Table 15 Effect of pH on Zinc Rejection

pH	Zn Concentration, mg/l		Gel Phase	Efficiency %	
	Feed	Raffinate	Expansion Ratio	Rejection	Uptake
9.4	24	28	67	42	--
11.3	23	10	60	--	71
12.5	23	3	42	--	90
13.1	26	7	31	--	93

As shown in Table 14, rejection efficiencies ranged from 30% at high feed concentrations (820 mg/l) to 70% at low feed concentrations (19 mg/l). Although the initial pH of all the feed solutions was essentially the same (7.9-8.1), the pH values of the raffinate were significantly different. Raffinates from the tests with high feed concentrations of zinc showed a drop in pH to 6.1 and 7.7; by contrast, pH of the raffinates from low zinc concentration feed solutions increased slightly (8.5-9.1). The gel expansion ratio was correspondingly lower. Gel expansion ratio defined as the weight of expanded gel divided by the weight of dry gel ranged from 32 at a raffinate pH of 6.1 to 72 at pH 9.1 with the low zinc concentration feed solution. This trend of higher expansion ratios at higher pH is consistent with the previously described effect of pH on gel expansion. However, the observed differences in pH were unexpected. Possible explanations are discussed below.

In view of the poor performance of the gels at high zinc concentrations and low pH, a series of tests were made to examine rejection efficiency of higher pH levels and using lower zinc feed concentrations. The lower feed concentrations were felt to be more realistic for wastewaters. Table 15 shows equally surprising results, namely, progressively lower expansion ratios and a dramatic change in rejection efficiency at pH 11.3 and higher. Whereas at pH 9 raffinate concentration was higher than feed concentration, the reverse was observed at higher pH. Zinc concentration of the raffinate was progressively lower clearly indicating that zinc was being removed from the solution phase and incorporated into the gel phase.

Optimal conditions for rejection of the zinc complex appear at approximately pH 9 as does the maximum gel expansion ratio.

Discussion

Lower gel expansion ratios observed with high concentration feed solutions are probably due to the high ionic strength of these solutions. As shown in Figure 26, expanded gel mass appears to correlate with the calculated ionic strength (μ) which is a measure of the product of ion concentration and charge

$$\mu = 1/2 \sum c\, z^2$$

where c = concentration M/l
z = ionic charge.

Ionic strength is almost directly proportional to zinc concentration because the solutions were prepared by dissolving zinc metal in excess HCl followed by neutralization with NaOH. Comparison with the results on the effects of salt concentration on gel expansion in Figure 16 shows the same trends, namely less gel expansion at high salt concentration. This suggests that ionic strength can be used to characterize gel expansion capacity. The effect of ionic strength has important practical implications. Gel capacity for absorbing water is reduced significantly which means that more gel would be required to achieve the same volume reduction.

The reduction in rejection efficiency with increasing feed zinc concentration (Table 14) can also be ascribed to the physical chemical effects of high ion concentrations. High ion concentrations tend to reduce ionic interactions, i.e., repulsion between like charges. Conceptually, this phenomenon accounts for lower repulsive forces between adjacent charged groups in the gel and hence less volume expansion as well as lesser repulsion of solution ions by the gel's ion atmosphere.

Comparison of the test results on zinc solutions with measured and calculated rejection efficiencies summarized in Table 10 for dye solutions show that the process effects are the same; increasing salt concentration reduces selectivity. It is interesting to note that Donnan equilibrium considerations can be used to predict the observed effects of salt concentration quantitatively. Donnan equilibrium does not invoke the shielding of electrostatic repulsion forces to account for the effects of salt concentration.

Uptake of zinc species at high pH conditions (Table 15) is probably not due to ionic effects per se even though gel mass volume data fit the same correlation line of gel volume versus log μ shown in Figure 26 for different concentration zinc solutions. Increasing pH (by adding NaOH) resulted in higher ionic strength and less gel expansion. However, this would not account for the dramatic change in selectivity.

The ability of expanded gels to retain zinc species is believed to reflect a change in chemical speciation. Increasing pH favors the formation of hydroxy complexes as shown in Table 13. At pH 11, $Zn(OH)^{+1}$ and $Zn(OH)_2^{\circ}$ predominate and Zn^{+2} is essentially absent. Furthermore, at pH > 11, calculations show that solid phase $Zn(OH)_2$ is produced even in the presence of $EDTA^{-4}$. This would account for the removal of Zn species from solution at high pH. It is not known whether the zinc species penetrate into the gel or accumulate as a precipitate on the surface of gel particles.

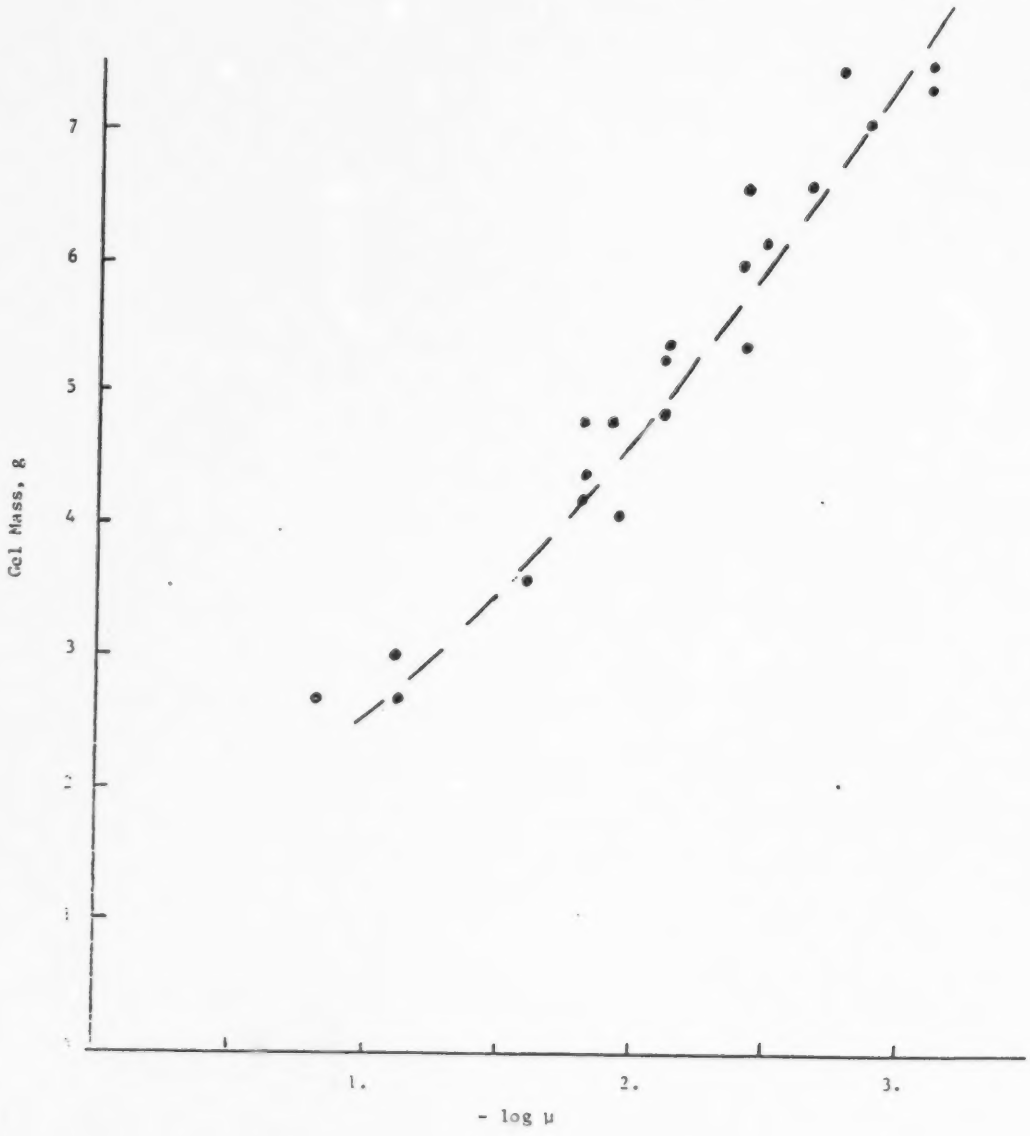


Figure 26 Gel Volume Versus Ionic Strength of External Solution

Solutions Containing Organic Solutes

Pentachlorophenol Chemistry

Separation of pentachlorophenol (PCP) was studied because it is a hazardous pollutant widely used as a wood preservative and pesticide; it has been identified as a major water-soil-aquifer pollutant at numerous sites throughout the U.S.; it serves as a model compound that is representative of a broad class of chemical compounds (chlorophenolics) that are of environmental concern. Removal of PCP and related chloroorganics from wastewaters and polluted sites is mandated by Federal and State laws. Improved technology for effective and low cost treatment would therefore be potentially useful in numerous situations.

PCP is only slightly soluble in water at low pH but highly soluble as the phenolate ion at high pH. pK is reported to be 4.71. Total solubility has been characterized as the sum of the concentration of protonated phenol (ϕ) and phenolate ion (ϕ^-) which is assumed to be highly soluble.

$$\text{Solubility} = \phi + \phi^-$$

where $\phi \dashrightarrow \phi^- + H^+$

$$K_a = \frac{[\phi^-][H^+]}{\phi}$$

Total solubility at pH 5.5 was found to be 10 mg/l. Using this measured value and the pKa value of 4.71, total solubility of PCP as a function of pH was calculated as shown in Table 16.

Table 16

Solubility of PCP vs pH

pH	5.5	6.0	7.0	7.5	8.0
Solubility mg/l	10	28.5	272	858	2710

Solubility of the unionized species is calculated to be 1.4 mg/l which indicates that PCP is essentially insoluble at low pH. Solubility phenomena have important practical implications in gel extraction because they affect rejection efficiencies.

Gel Extractions of PCP and Phenol

Aliquots (.06 g) of dry PAC-1 gel were contacted with 20 ml solutions PCP and allowed to equilibrate on a shaker. The gel phase was separated from the raffinate phase by draining through a fine mesh sieve. In some tests, light suction pressure was used to speed up and enhance phase separations. Raffinate phase and feed solutions were weighed and mass of water imbibed by the gel phase was calculated from a mass balance; it was measured directly in some case as a check on the accuracy of the mass balance approach. PCP concentration and pH

were measured in feed and raffinate solutions. As shown in Table 17, gel rejection efficiencies of PCP ranged from 40 to 62%; higher efficiencies were observed at lower feed concentrations. Gel expansion was carried out at pH 7 which is below the pH level for maximum gel expansion. Nevertheless, gel expansion ratios (expanded/dry gel weight) were high, ranging from 100 to 140.

The last column in Table 17 shows predicted rejection efficiencies based on Donnan Equilibrium calculations. Predicted rejection efficiencies are consistently higher than the measured values. However, the trend of lower rejection efficiencies with increasing solution concentration is the same.

Table 17

Higher Gel Rejection Efficiencies at Low Concentrations

Pentachlorophenol Concentration		Gel Rejection Efficiencies	
Feed	Raffinate	Measured	Donnan Calc*
mg/l	mg/l	%	%
1008	1246	47	72
504	655	41	85
105	148	54	96
49	71.7	62	98

* 12.3% ionizable monomers

Results obtained with phenol solutions are shown in Table 18. Phenol was not rejected from high feed solutions (> 25 mg/l) at pH 7.2. However, exclusion efficiencies of 40-67% were observed at pH 10.3; the trend of lower efficiency with increasing feed concentration is similar to that observed with PCP solutions (Table 17). Low concentration phenol (10 mg/l) was also rejected at pH 7.2.

Discussion of pH-pK Effects

Process performance of gels is affected by pH conditions in terms of the gel's expansion capacity as well as its rejection efficiency of ionic species. Detailed analysis of process conditions within and around the gel to determine the degree of ionization of the gel's potentially ionizable sites as well as the degree of ionization of solutes is therefore a prerequisite for characterizing solute rejection qualitatively and quantitatively.

With reference to the comparison of measured and predicted rejection efficiencies of PCP (Table 17), it should be noted that the predictions are based on the assumption that PCP is present as the phenolate ion and therefore assumed to be completely soluble. Furthermore, the calculations assume that all potential sites of the gel are ionized at the prevailing pH (7.0). Neither of these assumptions are entirely correct for a solution environment of pH 7. The gel is not fully expanded at pH 7 as a result of the fact that some carboxyl groups are still protonated. This is in accord with the gel's expansion behavior which reflects the gradual increase in pK with increasing degree of

ionization discussed previously. The effect of pH on PCP speciation is equally if not more important. Although phenolate ions are the preferred species at pH 7, (ϕ^-/ϕ = 200 based on pK) solubility of phenolate ions is limited to approximately 276 mg/l as shown in Table 16. It therefore appears that PCP was not completely solubilized and may have been present as a very fine suspension or as a supersaturated solution that was not rejected as effectively as phenolate ions.

The low rejection efficiency observed with phenol at pH 7.2 (Table 18) is consistent with the poor rejection of low molecular weight (small diameter) electrostatically neutral molecules described previously. Phenol has a pK of 9.9 which means that it is essentially not ionized at pH 7.2. At pH 10.3, 70% of the phenol is ionized and measured rejection efficiencies were correspondingly much higher (40-67%).

Table 18

Phenol Is Excluded at High pH*

Feed Concentration mg/L	pH	Exclusion Efficiency %	pH	Exclusion Efficiency %
50	7.3	3.	10.3	40
25	7.2	3.	10.3	54
10	7.2	36	10.2	67

* phenol pKa = 9.9

Effect of Gel Concentration

The related effect of changing the quantity of dry gel added per unit of feed solution volume was also tested. Increasing the amount of gel added increased the amount of water extracted resulting in higher raffinate concentrations as shown in Table 19. PCP feed solution (nominal 50 mg/l) was prepared with a minimum of sodium hydroxide in order to minimize ionic strength of the solution; pH was 6.3. The raffinate pH concentration (after equilibration with gel) increased to 8 indicating that the dry gel was more alkaline than the feed solution. It is interesting to note that mild extraction with small quantities of gel gave high rejection efficiencies that are in line with predictions based on Donnan equilibrium.

Effect of Salt Concentration

As indicated in the section on gel volume, the presence of salts reduces gel expansion. Theory predicts a similar effect on selectivity, i.e., that increasing salt concentration decreases rejection efficiency of ionic solutes. To test this prediction, a series of PCP feed solutions containing different concentrations of NaOH were prepared. NaOH was added to solubilize PCP; a

Table 19 Extraction Using Initially Dry Gel

Feed Solution:				Raffinate:			Gel:	
Dry Gel mass Added, g	PCP Conc(ppm)	NaOH Conc(mol)	pH	Mass(g)	Mass(g)	PCP Conc(ppm)	pH	Mass (g) Subtract	Rejection Efficiency(2)
.020	(1)	.0002	6.3	20.0	18.0	57.4	8	2.02	139% (99)
.040	(1)	.0002	6.3	20.0	16.0	63.3	8	4.04	109% (90)
.060	(1)	.0002	6.3	20.0	13.0	70.8	8	6.16	97% (84)
.080	(1)	.0002	6.3	20.0	11.5	80.6	8	8.58	84% (76)
.100	(1)	.0002	6.3	20.0	9.3	91.5	8	10.80	73% (67)

(1) Solute concentration measurement of 49.7 mg/l was based on a single measurement; it is believed to be in error as evidenced by the fact that calculated rejection efficiencies are greater than 100%.

(2) Efficiencies in parentheses were recalculated assuming feed concentration of 51.7 mg/l.

minimum of 0.00022 moles/l NaOH was needed for this purpose and resulted in a pH of 7.4. As shown in Table 20, increasing NaOH addition resulted in progressively higher pH values. The measured efficiencies were inversely related to NaOH added. The best efficiency was obtained with the lowest NaOH addition which gave a raffinate pH of 8.1 and also gave the largest gel volume expansion. Higher NaOH concentrations resulted in less volume expansion and lower rejection efficiencies.

Other Organic Chemicals

Gel extraction experiments were carried out with selected organic chemicals representative of important groups of pollutants, i.e., herbicides, pesticides, and solvents. The results are summarized in Table 21.

High rejection efficiencies were observed with 3,5 dichlorobenzoate (3,5-DCB) and 2,4-dichlorobenzoic acid (2,4-D). Benzene, dinitrobenzene, atrazine and alcohols except for tertiary alcohol were not rejected; none of these solutes are ionic. However, tertiary butanol may exhibit some ionic character (30).

Table 20 Effect of NaOH Concentration on PCP Rejection

	Feed Solution:						Raffinate:					
Expmt #	Dry Gel Added,g	Solute nom Conc(ppm)	Solute meas Conc(ppm)	NaOH nom Conc(mol)	pH	Mass(g)	Mass(g)	Solute meas Conc(ppm)	pH	Mass (g) substract	Mass (g) measured	Rejection Efficiency
(pentachlorophenol)												
40.1	.060	50	49.4	.00022	7.4	20.03	14.59	68	8.1	5.440	5.41	101%
40.2	.060	50	49.6	.0022	11.2	20	14.84	62.2	11	5.160	5.04	73%
40.3	.060	50	49	.0202	12.3	20.03	16.45	52.8	12.3	5.580	3.38	36%
40.4	.060	50	49.3	.1	12.9	22.25	19.87	52.1	12.9	2.380	2.22	47%
(control)												
41.1	.060	0	0	.0402	12.4	20.03	17.31	0	12.4	2.720	3.58	0%

Table 21

Exclusion Efficiency of Selected Industrial Chemical Structure

	Feed Conc. mg/L	Exclusion Efficiency	
3,5 Dichlorobenzoate (1)	50	70+	
	25	84	
2,4 Dichlorophenoxy acetate (1)	50	91	
	25	93	
	10	(100)	
Atrazine	25	0	
	10	0	
n-Butanol	50	V	
	25	V	
	10	V	primary alcohol
Iso Propanol	50	V	
	25	V	
	10	V	secondary alcohol
Tertiary Butanol	50	46	
	25	44	
	10	78+	tertiary alcohol
Benzene	50	46	
	25	0	
Dinitrobenzene	50	0	
	25	0	

(1) Detailed test results are listed in Table 22.
(V) Alcohols were not rejected consistently.

In this set of experiments, the pH of the feed solution was raised to 8-9 prior to addition of well washed dry PAC-1 gel. Washing was designed to remove residual alkalinity so as to reduce ionic strength of the gel phase. pH of the raffinate at the end of the test was 7.4, indicating that the well washed dry gel must have been less basic than the feed solution. Nevertheless, high rejection efficiencies were obtained.

Table 21 shows decreasing rejection efficiencies with increasing solute concentrations. This trend is consistent with PCP test results. It should also be pointed out that the salt concentrations in these tests were very low by minimizing addition of NaOH (< 0.0003 M/l).

Table 22 Gel Extraction of Solutions of Selected Industrial Chemicals

		Feed Solution:					Raffinate:			Gel:		
Expmt #		Solute nom Conc(ppm)	Solute meas Conc(ppm)	NaOH nom Conc(mol)	pH	Mass(g)	Mass(g)	Solute meas Conc(ppm)	pH	Mass(g) subtract	Mass(g) measured	Rejection Efficiency
(dichlorobenzoate)												
42.1	.060 g	50	48.36	.0005	8	29.871	23.932	71.11	7.4	5.939	5.557	190%
42.1	.060 g	50	48.36	.0005	8	29.887	24.051	56.57	7.4	5.836	5.668	70%
42.2	.060 g	25	24.34	.00025	8	29.906	24.054	28.13	7.5	5.852	5.655	64%
42.2	.060 g	25	24.34	.00025	8	29.875	23.91	30.66	7.4	5.965	0	104%
(dichlorophenoxy)												
43.1	.060 g	50	49.87	.0003	9.1	29.905	23.812	61.69	7.5	6.093	5.709	93%
43.1	.060 g	50	49.87	.0003	9.1	29.876	24.097	60.51	7.5	5.779	5.517	89%
43.2	.060 g	25	25.34	.00015	9.1	29.983	24.311	30.66	7.4	5.582	5.338	91%
43.2	.060 g	25	25.34	.00015	9.1	29.867	23.816	31.54	7.4	6.051	5.89	96%
43.3	.060 g	10	9.79	.00008	9.1	29.873	23.939	13.22	7.4	5.934	5.742	141%
43.3	.060 g	10	9.79	.00008	9.1	29.821	23.741	12.63	7.5	6.080	5.997	113%
(phenol)												
44.1	.060 g	50	49.75	0	8.5	29.836	23.918	49.75	7	5.918	5.751001	0%
44.1	.060 g	50	49.75	0	8.5	29.963	23.942	50.38	7.5	6.021	5.718001	5%
44.2	.060 g	25	25.62	0	8.7	29.838	24.26	25.93	7.1	5.578	5.426	5%
44.2	.060 g	25	25.62	0	8.7	29.85	23.724	25.62	7.3	6.126	5.715	0%
44.3	.060 g	10	9.63	0	8.6	29.892	24.078	10.73	7.1	5.814	5.619001	47%
44.3	.060 g	10	9.63	0	8.6	29.887	23.808	10.25	7.2	6.079	5.842	25%

Polymer Reuse

The cyclic reuse of polymer for extracting water from wastewater solutions is based on the premise that it is chemically and physically stable. Chemical stability implies that there is no irreversible chemical reaction that would impair the gel's capacity to expand and contract. Physical stability has to be defined with reference to each of the major steps in the overall process. This includes (a) method of contacting the collapsed gel and solution to be extracted, (b) method of acidifying the expanded gel and (c) physical separation process that is used to separate the gel phase from the raffinate phase or from the released water phase.

In order to give some insight on these questions, a series of cyclic tests were carried out. The objective was to determine whether there was measurable deterioration of the gel's properties as a result of cyclic reuse for extracting solutions that contain organics or trace metals.

An aliquot of Dextran gel (CM Sephadex C-50) was subjected to a series of 12 expansion and contraction cycles. This gel has a dry particle size of 60-120 μm, it is weakly ionic and was used as received. A dilute suspension of 34.6 nm polystyrene latex solution was contacted with the gel. After expansion it was removed and raffinate concentration was measured. Acid was added to collapse the gel and filtered to remove the released water. A drop of base was added to the gel filter cake, and again contacted with the raffinate. From a mass balance, the final raffinate concentration (c) after n treatment cycles, assuming perfect exclusion of the latex particles is given by:

$$C = \frac{m}{V_o - nV}$$

where m is the initial mass of latex, V_o is the initial volume of solution, and v is the volume removed by one treatment cycle of gel absorption. Thus the reciprocal of concentration c should vary linearly with the number of cycles n. The results for 12 cycles given in Fig. 27 show that this is the case for latex solutes. These results have two important corollaries. First, there is little cumulative loss due to latex adsorption on this gel. This suggests that adsorption which is responsible for the lower separation efficiencies reported in Table 9, is apparently most significant for the first cycle, and is less important as the gel is reused.

The second corollary of the results in Fig. 27 is that the gel is removing the same amount of water on the tenth cycle as on the first cycle. This implies that the gel's swelling capacity remains essentially constant over all cycles, and hence can be reused in cyclic operation. To be sure, reuse in practice will involve hundreds of cycles and such extensive long term tests have not been made.

Parallel sets of experiments were carried out using aliquots of polyacrylamide gel (PAC-1) to extract solutions containing 2,4-D and EDTA-Zn. The gels were regenerated by acidifying with HCl. The experiments were plagued with mechanical problems so that the results are inconclusive. There appears to have been some loss of gel due to handling. The PAC-1 gel was structurally weak even though it was made with 5% crosslinking agent. As a result, small pieces of gel were removed with the raffinate. There was no measurable indication of changes in rejection efficiency.

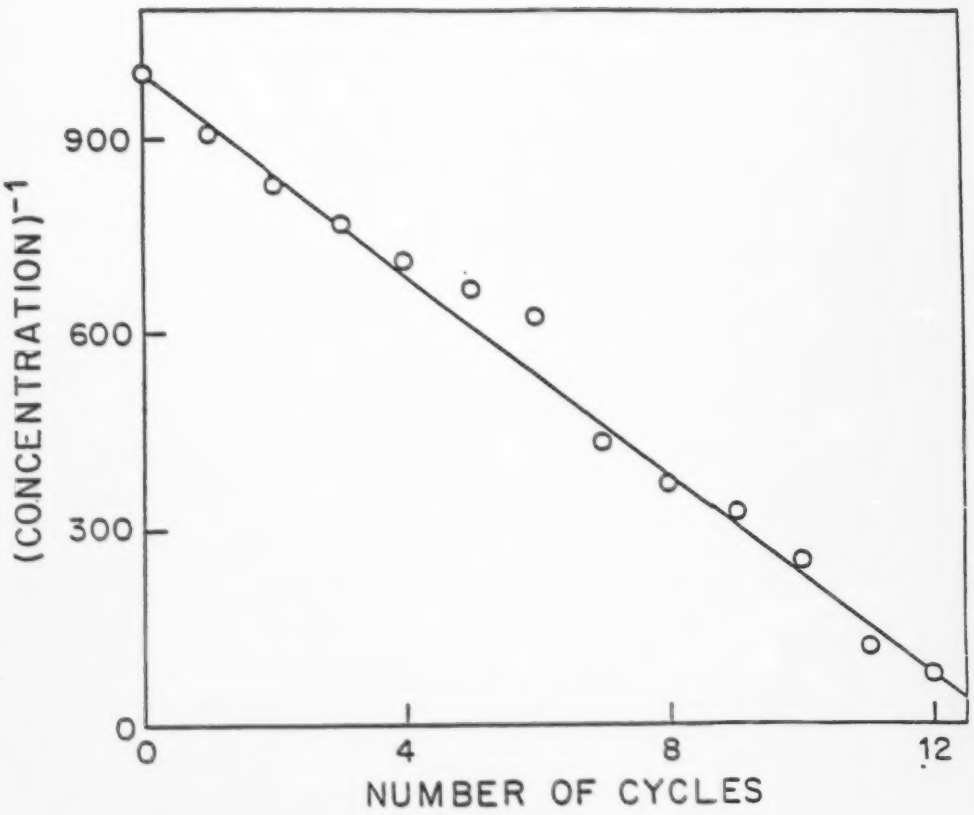


Figure 1: Latex Concentration over Several Gel Extractions.

CO_2 Acidification

In order to avoid using mineral acids for acidifying the swollen gels, a short experiment was carried out to measure the effectiveness of using pressurized carbon dioxide. Swollen gel was treated with carbon dioxide at a pressure of 2 atmospheres. Carbon dioxide goes into solution to form carbonic acid which undergoes dissociation.

$$CO_2 + H_2O \text{ ---> } H_2CO_3 \text{ --- } HCO_3^- + H^+$$

Equilibrium pH was calculated from Henry's law constant for CO_2 in water and acid dissociation constants from the literature (38); at 2 atmosphere partial pressure the pH is 3.7. The advantage of using pressured CO_2 to reduce pH is that it avoids salt accumulation. CO_2 related acidity is neutralized by depressurizing which reverses the reactions shown above.

Some contraction of gel volume was observed in a short time exposure to 2 atmosphere of CO_2. However, the gel was not completely collapsed. Further testing would be needed to determine whether CO_2 acidification is practical.

Process Design Considerations

Laboratory studies to define the properties of water soluble polyacrylamide gels and modified gels as extraction agents have been described in previous chapters. Two categories of gels have been tested. Partly hydrolyzed polyacrylamide gels were evaluated because they are potentially polyvalent and have the capacity to reversibly imbibe and expel large volumes of water in response to imposed changes in pH. Modified acrylamide polymers are largely nonionic. They have the capacity to reversibly imbibe and expel water in response to small changes in temperature. Both classes of gels can be used to extract water from solutions and to reject certain types of solutes. However, the hydrolyzed polyacrylamide gels also exclude (reject) negatively charged solutes by electrostatic repulsion and reject large molecules because of stearic effects. Temperature sensitive gels reject large size molecules due to stearic effects, i.e., molecules that are larger than the openings of the polymer skeleton are prevented from entering. Design criteria for both types of gels have been outlined.

Ionic-pH Sensitive Gels

Charge density is the driving force that actuates gel expansion and regulates entry of ionic species into the gel phase. Process variables that affect charge density include gel composition as well as solution chemistry. Crosslinker and initial monomer concentration are the major gel manufacturing process variables. Maximum volume expansion ratio V/md to the -2/3 power correlate with concentrations of crosslinker and acrylamide that are used in making the gels. This correlation can be used to design the desired water extraction capacity per unit weight of dry gel. Strength and hence ease of handling of the gel are limiting factors. Almost all the gel formulations have large potential volumetric expansion ratios so that maximizing expansion ratios is probably not the most important design consideration. However the degree of hydrolysis may be important as shown below.

Laboratory process studies have demonstrated that ion exclusion effects can be explained in terms of a Donnan equilibrium model. This model was therefore used to calculate the equilibrium distribution of ions between the raffinate phase and the expanded gel phase as shown in Figure 28. Concentration of solute ions in the gel phase are directly related to the raffinate concentration with the percent ionizable groups as a parameter. Percent ionizable groups is expressed as % of monomers because polyacrylamide has one carboxyl group per monomer so that the ultimate potential concentration of ionizable groups is equal to the monomer concentration. Increasing % of monomers ionized causes greater rejection of ionic solutes from the gel phase and results in higher raffinate phase concentration.

% rejection was calculated from:

$$\frac{\text{Raffinate conc. - gel phase conc. x 100}}{\text{Raffinate conc.}} = \text{\% Rejection}$$

Lines representing 0, 90, and 99% rejection are shown in Figure 28. They illustrate the advantage of using gels that are highly ionized. The graph also shows that separation is most effective at low concentrations. In fact, it is theoretically impossible to achieve very low gel phase concentrations with high raffinate concentrations.

The correlations presented in Figure 28 provide a convenient tool for process design calculations for ionic solutes. The "% of monomers ionized" parameter is both a measure charge density in the gel phase and a measure of the quantity of acid and base needed to actuate the gels' expansion-contraction cycles. Ultimate charge density depends on the degree of hydrolysis of amide groups into carboxyl groups. Complete hydrolysis increases rejection efficiency but results in large acid base requirements. The quantity of acid-base needed per cycle can be calculated from the % of monomers ionized. The quantity of acid-base needed for pH adjustment is small and can usually be neglected.

The acid-base addition is not likely to cause problems in treating low concentration wastes in a single stage. Nevertheless, each expansion-contraction cycle does increase salt concentration of the liquid phases on neutralization. This could be an important factor in processes using staged separation that involve several expansion-contraction cycles in series.

Temperature Sensitive Gels

The development and utilization of modified polyacrylamide gels that swell and contract in response to small changes in temperature while rejecting large solute molecules has been briefly investigated as a separation process for treating wastewaters. Laboratory test results (described in previous chapters) demonstrate the feasibility for separating large molecular weight solutes. Furthermore, it may be possible to change the gel's rejection capacity and efficiency by modifying the gel's structure. Changing crosslinking concentration has been shown to give better separation of smaller solutes. However, there is no abrupt molecular size cut-off. The random distribution of mesh sizes of a crosslinked polymer is expected to give a range of molecular size separations.

The major advantage of the temperature sensitive gels is that the need for chemicals (acid-base) is eliminated. Composition and chemistry of the solutions is therefore not changed. Energy requirement is a process consideration and is briefly discussed below.

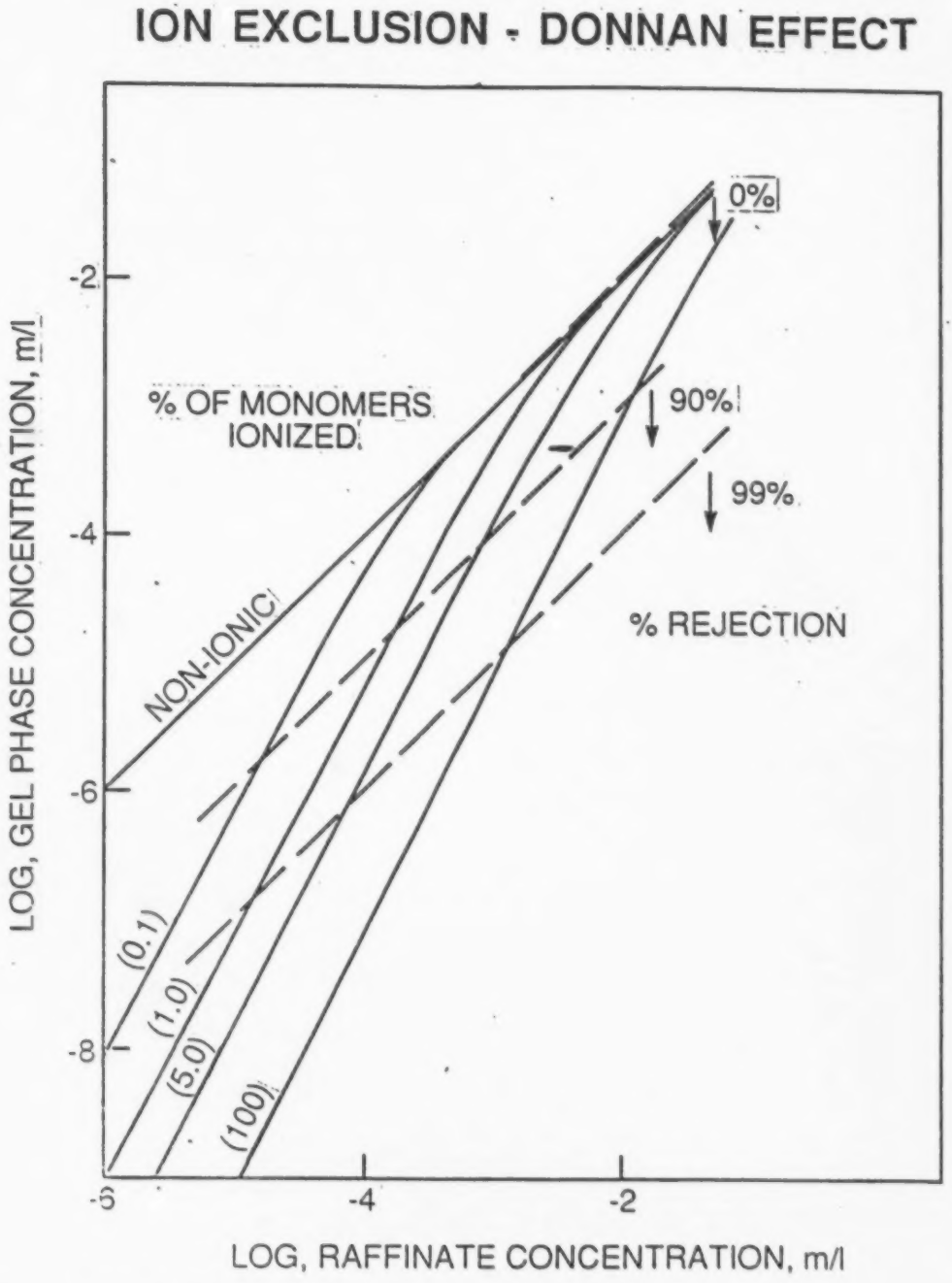

ION EXCLUSION - DONNAN EFFECT
0%
90%
99%
% OF MONOMERS IONIZED
% REJECTION
NON-IONIC
(0.1)
(1.0)
(5.0)
(100)
-2
-4
-6
-8
-6
-4
-2
LOG, GEL PHASE CONCENTRATION, m/l
LOG, RAFFINATE CONCENTRATION, m/l

Figure 28

Extraction capacity of temperature sensitive gels is probably not as large as that of equivalently crosslinked ionic gels. Nevertheless, expansion ratios are sufficiently large so that gel requirements are not expected to be controlling design considerations.

Energy Requirements

Energy requirements are relatively low compared to alternative separation schemes as illustrated in the following example drawn from the work of Freitas (27,31). The calculations are based on removing half the water from a solution of 0.1 moles of solute in 10 moles of water. The minimum of energy needed to removed half the water is equal to the negative Gibbs free energy of mixing. For an ideal solution this comes to 40 cal.

Separation using gels would require raising the temperature to collapse the swollen gel in order to release the water. The energy required for heating is calculated from the molar heat capacity of water and the maximum temperature increase. Assuming a 10°C change in temperature, the calculated energy requirement is 900 calories for extracting 5 moles of water (90 g). It is important to note that this is low level energy that would be readily available as rejected heat from industrial and power generating facilities. Energy costs are expected to be low.

As a further illustration of the unique feature of the gel extraction process for extracting pure water, it is interesting to note that the energy required to evaporate the same amount of water from solution would require 50,000 calories of higher level energy.

SECTION 9

SUMMARY - CONCLUSION

This report describes the results of a study aimed at developing a new extraction process for dewatering dilute aqueous solutions. Water soluble gels that form a separable gel phase are used to extract water from solutions while rejecting solutes thereby concentrating solutes in the raffinate. Two types of gels have been developed and tested.

Ionic gels which consist of partly hydrolyzed crosslinked polyacrylamide gels, have been shown to reject solutes by size as well as due to electrostatic repulsion. Gel phase volume expands at high pH by imbibing water; it contracts and expels water at low pH. A typical processing sequence is shown in Figure 3. Each complete cycle separates feed solution into a purified water phase, a more concentrated raffinate phase, and a collapsed gel phase in response to changes in pH. pH changes are induced by acid and base additions with attendant changes in ionic charges of the gel's carboxyl groups. Changes in charge density actuate the gels' capacity to expand by imbibing water and to contact by expelling water.

Temperature sensitive gels which consist of crosslinked polymers of modified acrylamides are non-ionic. Expansion and contraction of the gel phase is in response to small changes in temperature. These gels reject solutes by size only and are therefore more useful for separating large molecules or colloids. A typical process cycle is illustrated in Figure 2.

The physical chemical properties of polymers and gels have been studied in the context of their application for extraction of chemical solutions encountered in wastewater treatment and aqueous hazardous waste management. Chemical formulation of polymers was investigated with a view to maximizing gel expansion (water extraction capacity) and rejection efficiency of solutes. Concentration of crosslinking agent and the concentration of acrylamide monomer in the reaction mixture have been shown to be important variables. Subsequent hydrolysis of the polymerized acrylamides into carboxyl groups is also a major variable because it determines the gel's maximum potential charge density.

Process studies to measure water uptake capacity and solute rejection efficiencies were carried out with different solutes over a broad range of concentrations. The more important findings are listed below.

As regards effects associated with the chemical formulation of the gel:

(a) Increasing the concentration of crosslinking agent decreases expansion capacity and reduces the volume of water extracted per unit mass of polymer.
(b) Increasing the concentration of monomer during polymerization has the same effect.
(c) Increasing the degree of hydrolysis increases potential charge density; this is expected to increase expansion potential.
(d) Solute rejection efficiency is enhanced at high charge density and high cross link concentration.
(e) Temperature response of the gels made form substituted acrylamide monomers is related to the chemical nature of the substituent; polyisopropylacrylamide responds at lower temperature than diethyl acrylamide. Critical solution temperature effects have been invoked to explain the observed effects. However, detailed mechanistic explanations have not been worked out. Additional studies are needed to more fully explore the potential for making gels that respond to different temperature changes.

As regards the effects of processing conditions:

(f) pH is the dominant variable with ionic gels; it regulates charge density within the gel and hence the dynamics of expansion and contraction. Increasing pH results in gel expansion and vice versa. Measured changes in volume are in accord with model predictions based on electrostatic repulsion forces in a polymer matrix.

(g) Ionic strength of the solution phase is an important variable in so far as it affects the electrostatic repulsion forces of point charges in the gel and the sphere of influence of solute ions. Increasing ionic strength reduces the gel's expansion capacity; it also reduces the gel's rejection efficiency of charged solute species. The effects of ionic strength on rejection efficiency can be described by a Donnan equilibrium model that treats the distribution of ions between the gel phase and the exterior solution phase in terms of a membrane separation. Model predictions are in accord with measured separations and provide a useful framework for making quantitative predictions.

(h) At ionic strength below 1.0 there was very little effect on temperature sensitive gels.

(i) Complete separation of raffinate from the expanded gels phase is important; entrainment of raffinate between gel particles compromises the rejection efficiency.

As regards the effects of solute chemistry:

(j) Large size molecules are rejected by both types of gels. Size exclusion of solutes is determined by the mesh size of the polymer skeleton which is affected by the gel's crosslinking and polymer density. The efficiency of exclusion does not show an abrupt change with molecular size which is consistent with a random distribution of mesh sizes of crosslinked polymers.

(k) Valence charge on the solute is a critical variable with ionic gels. Multiple charge solutes are rejected more effectively than monovalent solutes.

(l) pH effects on solute charge were observed in two ways. Ionic species resulting from proton dissociation were not rejected at pH values below the pKa of the solute. With mixtures of EDTA-Zn complexes and zinc ions, the formation of neutral species or positively charged species resulted in uptake of zinc by the gel phases and attendant depletion of zinc in the raffinate phase.

(m) Rejection efficiency is also influenced by pH changes in so far as the solute is subject to precipitation at either high or low pH. As an example, precipitation of PCP occurs when solution pH drops below 7 and is believed to be responsible for low rejection efficiencies at low pH.

(n) Theory and experimental measurements show that higher rejection efficiencies are obtained at low feed concentration. Essentially complete rejection of solutes would probably require staged operations.

(o) Regeneration and reuse of gels has been demonstrated. Although the laboratory testing involved a relatively low number of complete cycles, commercial experience with gels in chromatographic separation indicates that they are both physically and chemically stable.

(p) Process information on chemical requirements (acid-base), energy requirements (heat) and gel requirements (water extraction capacity of gels) have been described.

SECTION 10

FUTURE WORK

The dynamics of swelling and contraction should be studied. The work described in this report was designed to analyze and describe water extraction capacities and rejection efficiencies at equilibrium. The time rate of change of gel expansion and contraction has not been studied. It has been observed that gel volume changes are very fast for small aggregates of gel. However, rates of water movement and exchange of ions by larger aggregates of gel should be studied in order to define mass transport limitations. A better understanding of the effects of gel aggregate size is needed in order to optimize process design conditions for contacting during the expansion and contraction cycle.

Modified gels should be developed that combine the swelling and contraction characteristics of temperature sensitive gels with the solute rejection characteristics of the ionic gels. Such gels would be capable of rejecting ionic species as well as separating by molecular size. There are several advantages to using temperature cycles instead of pH changes to extract water; energy costs are low, there is no need for chemical addition, there is no increase in salt (ions) concentration.

Process studies to evaluate the effects of staging should be carried out. Single stage extractions that involve large differences in concentration between gel phase and raffinate are thermodynamically unfavorable. Staged or sequential extraction would be more efficient and allow for more complete rejection of solutes from the extracted water phase.

REFERENCES

1. Ilavsky, M., J. Hrouz, and K. Ulbrich, "Phase Transition Swollen Gels III: The Temperature Collapse and Mechanical Behavior of Poly(N,N-diethylacrylamide) Networks in Water," Polymer Bull., 7, 107 (1982).

2. Tanaka, T., "Collapse of Gels and the Critical Endpoint," Phys. Rev. Lett., 40, 820-823 (1978).

3. Tanaka, T., "Gels," Sci. Am., 224, 124 (1981).

4. Andrade, J. D., Hydrogels for medical and related applications, ACS Symposium Series No. 31, Washington, 1976.

5. Rathner, B.D. and A.S. Hoffman in Hydrogels for Medical and Related Applications, edited by J.D. Andrade, ACS Symposium Series, No. 31, Washington, 1976.

6. Cussler, E. L., M. R. Stokar and J. E. Varberg, Gels as Size selective extractive solvents, AIChE J., 30, 578, 1984.

7. Hasa, J. and M. Ilavsky, Deformational, swelling, and potentiometric behavior of ionized poly (methacrylic acid) gels. II Experimental results, J. Poly. Science, 13, pp. 253-262, 1975.

8. Ilavsky, M., Macromolecules, 15, pp. 782-788, 1982.

9. Tanaka, T., I. Nishio, S.T. Sun, and S. Ueno-Nishio, Collapse of gels in an electric field, Science, 218, pp. 467-469, 1982.

10. Tanaka, T., D. Fillmore, S. T. Sun, I. Nishio, G. Swislow, and A. Shah, Phase transitions in ionic gels, Phys. Rev. Letters, 45, pp. 1636-1639, 1980.

11. Fisher, L., Gel filtration chromatograph. Elservier Press, NY, pp. 205-231, 1980.

12. Ilavsky, M., Effect of Electrostatic interactions on phase transition in the swollen polymeric network, Polymer, 22, pp. 1687-1692, 1981.

13. Flodin, P., B. Gelotte, and J. Porath, A method for concentrating solutes of high molecular weight, Nature, 188, pp. 493-4, 1960.

14. Determan, H., Gel chromatography, Springer-Verlag, NY, pp. 56-60, 1980.

15. Dusek, K. and D. Patterson, Transition in swollen polymer networks induced by intramolecular condensation, J. Poly. Science A2, 6, 1209-1216, 1969.

16. Tanaka, T., Physical Review Letters, 40(12), pp. 820-823, 1978.

17. Dusek, K., Inhomogeneities induced by crosslinking in the course of crosslinking copolymerization, in Polymer Networks: Structural and Mechanical properties.

18. Hasa, J. M., M. Ilavsky and K. Dusek, Deformational swelling, and potentiometric behavior of ionized poly (methacrylic acid) gels. I. Theory, J. Poly. Science, 13, pp. 253-262, 1976.

19. Ilavsky, J., J. Hrouz and K. Dusek, Inhomogeneities and deviations from the gaussian photoelastic behavior of networks, J. Macromol. Sci., B19, pp. 227-236, 1981.

20. Flory, P.J., Principles of Polymer Physics, Cornell, Ithaca, 1979.

21. Hill, T.E., Statistical thermodynamics, Addison-Wesley, Reading, MA, pp. 410-419, 1960.

22. Andrews, G. P., The Effect of crosslinking on Extractions Using Polyacrylamide Gels, Thesis, University of Minnesota, 1985.

23. Kale, K. M., Cussler, E. L. and D. F. Evans, Characterization of Micellar Solutions Using Surfactant Ion Electrodes, J. Phys. Chem. 84, 593, 1980.

24. Gehrke, S. H., Gels as Selective Extraction Solvents, Ph.D. Thesis, University of Minnesota, 1985.

25. Gehrke, s. J., Andrews, g. P., and Cussler, E. L., Chemical Aspects of Gel Extraction, submitted for publication.

26. Rodriguez, F., Principles of Polymer Systems, McGraw Hill Book Co., NY, 1982.

27. Freitas, R.F.S., Extractions With and Phase Behavior of Temperature Sensitive Gels, Thesis, University of Minnesota, 1985.

28. Stokar, M. R., Gels as Size Selective Extraction Solvents, M.S. Thesis, University of Minnesota, 1982.

29. Mandel, M., The Potentiometric Titration of Weak Polyacids, European Polymer Jour., 6, 807-822, 1970.

30. Fieser, L. F. and Fieser, M., Organic Chemistry, Heath and Co., Boston, 1944.

31. Freitas, R.F.S. and Cussler, E.L., Temperature Sensitive Gels as Extractive Solvents.

32. Myers, D.W., Bowman, W.A., and Gabbert, K. E., New Microgel Colloids for the Study of Aqueous Polymer-Solvent Interactions, Paper #143, 5th International Conference on Surface and Colloid Science, Clarksen University, Potsdam, NY, June 25, 1985.

33. Robinson, R.G. and Stokes, R. H., Electrolyte Solutions, Butterworth, London, 1960.

34. Tanford, C., The Physical Chemistry of Macromolecules, Wiley, NY, 1961.